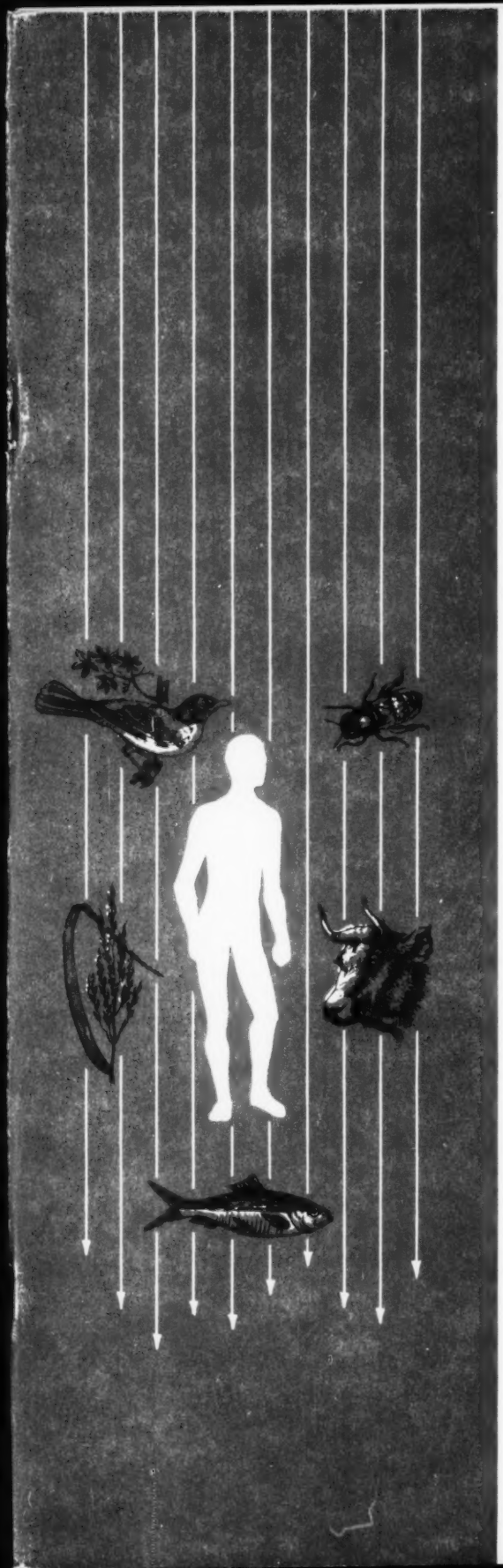

# PESTICIDES MONITORING JOURNAL

JUNE 1972

VOLUME 6 NUMBER 1

PEMJAA 6(1) 001-077 (1972)

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# PESTICIDES IN PEOPLE

## *DDT and DDE Residues in Blood From Children, South Carolina—1970*

Julian E. Keil,[1] William Weston, III,[2] C. Boyd Loadholt,[3]
Samuel H. Sandifer,[1] and James J. Colcolough [4]

ABSTRACT

*DDT and DDE residue levels in blood plasma from 192 children in South Carolina, ages 6-9 years, indicated that Negro children had levels two to three times higher than white children. DDT residues averaged 18.4 ppb in Negroes ond 6.7 ppb in whites; DDE values for these two races were 55.6 ppb and 24.8 ppb, respectively. White males in this group also had significantly higher levels of both compounds than white females. From the data in this study, baseline levels for a high-risk pediatric group, usually prone to pesticide poisoning, were established.*

### *Introduction*

In 1969, the S. C. Community Pesticide Study measured pesticide residues in plasma from 800 persons in Charleston County; the subjects had been selected by sex, race, residence, and 10-year age groupings (*6*). The outstanding findings of this study were: (1) Negroes had much higher levels of DDT and its metabolites than whites, and (2) children between the ages of 5 and 10 years had significantly higher DDT/DDE levels than the rest of the population studied and, in some instances, as high as DDT formulators.

The present study, partially reported here, was begun with several purposes in mind: (1) to confirm earlier findings of the South Carolina investigators of higher DDT and DDE levels among children and Negroes; (2) to establish new baselines for young children who are prone to poisoning, because analytical methods have changed since the earlier work; and (3) to explore reasons for the age and racial differences previously reported. This last endeavor is still under study.

### *Sampling Methods*

A total of 192 apparently healthy children, ages 6-9 years from public and private schools in Charleston, S. C., were stratified by race (nonwhites were almost exclusively Negro), sex, residence, and 1-year age spans. After approval by school authorities, written parental permission was obtained for blood sampling of the children. Venous blood samples were collected in heparinized vacutainers. Residue values for this group were compared with those of control subjects of the S. C. Community Pesticide Study.

### *Analytical Procedures*

Plasma extraction was carried out by a modified method of Dale, Curley, and Cueto (*1*), as recommended by the Perrine Primate Research Branch Laboratory in Perrine, Fla. Two milliliters of plasma were placed in a 16 x 125 mm round-bottom culture tube fitted with screw caps, size 15-415 with Teflon-faced liners; 6 ml of nanograde hexane were added; and the mixture was rotated on a slow speed rotating mixer at 50 rpm for 2 hours. The formation of emulsions was infrequent; when they did occur, centrifugation was used to separate the layers. Following the 2-hour rotation period, a 5-ml aliquot of the hexane layer was quantitatively transferred to a 10-ml graduated concentrator tube. The degree of concentration or dilution that was necessary was determined by a preliminary analysis of the 5-ml aliquot. If concentration was necessary, one 3-mm glass bead was added, and a modified micro-Snyder column was attached. The extract was evaporated on a steam bath to a volume of about 200 $\mu$l. The tubes

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were allowed to cool for about 5 minutes, the micro-Snyder column was removed, and the sides of the tube and column joint were rinsed down with hexane. The final volume was adjusted to 500 $\mu$l for subsequent analysis.

No celanup procedure was required or utilized. A 5 $\mu$l portion was then injected into a MicroTek 220 gas chromatograph equipped with a tritium foil electron capture detector. All injections were off-column injections. All samples were analyzed on the OV-17/QF-1 column, and the residues were confirmed on the SE-30/QF-1 column. It was necessary in almost all cases to run several sample extract chromatograms of various concentrations to achieve reasonable approximation of peak sizes with those of the standard mixture. The samples were stoppered and mixed on a Vortex mixer for about 30 seconds after each dilution before injection.

GAS-LIQUID CHROMATOGRAPHY

The operating parameters for gas chromatographic analysis were as follows:

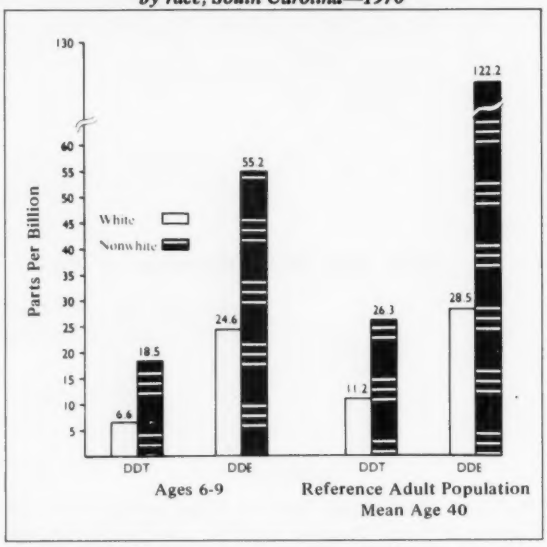
| | | |
|---|---|---|
| Columns: | 1.5% OV-17 and 1.95% QF-1 on Chromosorb W, DMCS, HP, 100/120 mesh; 4% SE-30 and 6% QF-1 on Chromosorb W, DMCS, HP, 100/120 mesh | |
| Temperatures: | Injection chamber | 225° C |
| | Column | 200° C |
| | Transfer block | 235° C |
| | Detector | 205° C |
| Nitrogen flow: | OV-17/QF-1 | 60 ml/min |
| | SE-30/QF-1 | 80 ml/min |

All qualitative retention times were based on the retention time of aldrin. Quantitation of pesticide residues was based on . ative peak areas which were supplied by an Infotronics Chromatograph Integrator Model CRS-101. Recovery, based on the addition of a known quantity of *p,p'*-DDE and *p,p'*-DDT, ranged from 95.0 to 98.6%. Residue results were not corrected for recovery. The minimum reporting limit for *p,p'*-DDE was 1.0 ppb and for *p,p'*-DDT, 2.0 ppb. No polychlorinated biphenyls were detected in any of the samples analyzed. A least squares analysis was used to estimate and test differences between strata means.

## *Results and Discussion*

Results of previous studies indicating unusually high DDT/DDE levels in preadolescents were not confirmed. As shown in Fig. 1, children in the 6-9 age group had lower levels than did their adult counterparts (control subjects of the S. C. Community Pesticide Study). This is at variance with earlier work by Finklea *et al.* (*6*), but consistent with results reported by Watson *et al.* (*7*). Improvements in analytical techniques since the earlier study (*6*) may have reduced variances in results and accounted for the lower levels.

FIGURE 1.—*Mean plasma levels of p,p'-DDT and p,p'-DDE in a pediatric group and adult reference group by race, South Carolina—1970*




DDT and DDE were two to three times higher in the Negro than in the white group. This difference was evident in the juvenile cohorts as well as in the adult reference group (Fig. 1). This study confirms racial differences in DDT/DDE residue levels between whites and nonwhites reported by Davis (*2,3*), Edmundson (*4,5*), and Finklea (*6*).

White males had significantly higher levels of both compounds than white females (Table 1). No significant differences in levels of DDT or DDE were apparent when sex and race were evaluated according to the place of residence of subjects (Table 2); thus, values in Table 1 may be used to estimate "normal" ranges for this high-risk pediatric age group, unusually prone to pesticide poisoning.

Table 3 lists DDT and DDE levels by 1-year age groups and indicates no significant increase or decrease in levels with age.

TABLE 1.—*DDT and DDE residue levels in plasma from 192 children, ages 6-9 years, by race and sex, South Carolina—1970*

| Compound | White* | | | Nonwhite | | |
|---|---|---|---|---|---|---|
| | Male (N=50) | Female (N=46) | SD[1] | Male (N=45) | Female (N=51) | SD[1] |
| DDT (ppb) | 8.5 | 4.8 | 6.5 | 16.9 | 19.7 | 11.0 |
| DDE (ppb) | 29.9 | 19.2 | 14.2 | 55.2 | 55.9 | 29.5 |

[1] Pooled standard deviation for sex within races.
* Differences between levels in white males and females significant at $P < .01$.

TABLE 2.—*DDT and DDE residue levels in plasma from 192 children, ages 6-9 years, by residence, race, and sex, South Carolina—1970*

| Race and Sex | Mean Residue Levels (ppb) | | | |
|---|---|---|---|---|
| | Urban | | Rural | |
| | DDT | DDE | DDT | DDE |
| White Males | 7.8 (N=27) | 28.2 | 8.9 (N=23) | 31.0 |
| White Females | 4.8 (N=24) | 16.9 | 4.7 (N=22) | 21.8 |
| Nonwhite Males | 16.5 (N=25) | 54.5 | 17.7 (N=20) | 54.5 |
| Nonwhite Females | 19.1 (N=27) | 49.2 | 20.5 (N=24) | 63.5 |

TABLE 3.—*DDT and DDE residue levels in plasma by age of 192 school children, Charleston County, S. C.—1970*

| Age (Years) | Mean Residue Levels (ppb) | |
|---|---|---|
| | DDT | DDE |
| 6 (N=35) | 14.5 | 41.5 |
| 7 (N=35) | 13.4 | 43.4 |
| 8 (N=42) | 11.9 | 38.1 |
| 9 (N=70) | 11.7 | 38.5 |

See Appendix for chemical names of compounds discussed in this paper.

This study was supported by EPA contracts PH21-2017 and NEG 68-03-0045 and by the Department of Pediatrics of the Medical University of South Carolina.

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# *Organochlorine Pesticide Residue Levels in Human Milk—Victoria, Australia—1970* [1]

K. G. Newton and N. C. Greene

ABSTRACT

*Samples of human milk were collected in 1970 from 39 rural and 28 urban donors in Victoria, Australia, and were analyzed for organochlorine pesticides using electron capture gas chromatography. All samples contained DDT, DDE, and HCB. Twenty-nine contained dieldrin (mean 0.006 ppm), 12 contained DDD (mean 0.007 ppm), and 3 contained both dieldrin and DDD. Total DDT averaged 0.139 ppm for rural 0.145 ppm for urban donors, and HCB averaged 0.042 ppm and 0.063 ppm, respectively.*

## *Introduction*

The Australian State of Victoria has a population of 3.4 million, 2.2 million of whom live in the capital city of Melbourne. The State is self-sufficient in food production; its agriculture, sophisticated and in parts intensive, supplies centralized common markets which distribute food throughout the metropolis.

The use of DDT, aldrin, dieldrin, and other common organochlorine pesticides is restricted to those situations where no suitable alternative is available, and tolerance limits set by State health regulations are low. Over the past 10 years, greater use has been made of the less persistent organophosphate and carbamate pesticides.

In an effort to determine organochlorine pesticide residue levels in human milk, a small survey involving 23 participants (13 rural and 10 urban) was carried out in April 1970. The rural donors lived on or near fruit orchards in Shepparton, the center for a district which produces under irrigation large quantities of tree fruits for the local and export markets. The donors were asked to collect milk during one or more feedings until about 2 ounces was obtained. Simple details on past exposure to pesticides were considered desirable but are not included with the results in Table 2, since efforts to obtain reliable information were unsuccessful.

Differences in the levels of total DDT between the two groups were apparent; however, it was determined that further sampling of other rural areas should be undertaken and that, to maintain parity, more metropolitan samples should be analyzed before valid conclusions could be drawn regarding such differences. A second survey consisting of 26 rural and 18 urban donors was undertaken in December 1970. These donors were selected with on consideration of age, race, weight, medical history, or age of baby.

Resources sufficient to guarantee an accurate history of pesticide exposure and uniform sample collection from each donor were not available. Thus, no exposure information was requested, and the mothers were relied on to collect their own samples according to a designated procedure which was simple enough to ensure cooperation and yet provide a representative sample.

This procedure was established after a preliminary study using one donor to obtain a limited check on variability in fat content of milk during the suckling period. In this study the mother collected a small amount of milk from several feedings at three intervals during each feeding, the beginning, middle, and end. Individual samples taken at each of these intervals were composited by group to provide three samples for analysis, and the results are shown in Table 1. These figures are not included in the general results.

## *Sampling Procedure*

Based on results of the preliminary tests to assess variability in fat content of the milk, the sampling procedure

[1] From the State Health Laboratory, 5 Parliament Place, Melbourne, Victoria, Australia 3002; permission to publish this paper was granted by the Chief Health Officer of Victoria.

TABLE 1.—*Organochlorine pesticide residue levels in human milk from one donor obtained at three intervals during each of several feedings*

| Time During Feeding | Percent Fat | Organochlorine Pesticide Residue Levels (PPM) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Total DDT | | HCB | | Dieldrin | |
| | | Whole Milk | Fat Basis | Whole Milk | Fat Basis | Whole Milk | Fat Basis |
| Beginning | 1.8 | 0.014 | 0.78 | 0.005 | 0.25 | 0.002 | 0.11 |
| Middle | 1.2 | 0.007 | 0.58 | 0.003 | 0.25 | 0.001 | 0.08 |
| End | 5.1 | 0.066 | 1.29 | 0.024 | 0.47 | 0.006 | 0.12 |

described below was followed. Written instructions were given to the volunteers asking them to combine over four to six feedings small quantities of milk taken alternately at the beginning and end of each feeding and to store the samples under refrigeration. A composite milk sample was obtained only once from each donor. Clean glass bottles with aluminum foil-lined caps, preprinted labels, and insulated packing cartons were supplied.

### *Analytical Procedure*

All samples were received in a fresh condition, freeze-stored until ready for analysis, and then thawed at room temperature. The milk was well mixed before aliquots were withdrawn.

All solvents were redistilled in glass before use and tested in conjunction with the other chemical standards for extraneous peaks. The unactivated Florisil used in sample cleanup was "1200 F" Florisil, from supplier's stocks, stored under room conditions. This Florisil was activated by heating at 650° C for 1 hour and stored at 130° C.

Fat was determined by the Gerber method (*8*) on a separate 11.0-ml aliquot. Chlorinated hydrocarbon pesticide residues were determined by modified procedures of Giuffrida *et al.* (*6*) for separating the fat and Mills et al. (*7*) for the cleanup.

Depending on the amount of milk available, 20 to 50 g was weighed into a 350-ml glass-stoppered flask, 100 ml of acetone and 20 g of celite were added, the contents shaken well, and then suction-filtered through a coarse paper. The retained milk solids and celite were returned to the flask and shaken with 100 ml of hexane and re-filtered. The combined filtrates were transferred to a 1-liter separating funnel and shaken for 30 seconds; 300 ml of water and 10 ml of saturated NaCl were then added and the funnel shaken again for 1 minute. The aqueous layer was discarded, and the dried hexane-fat solution evaporated to 5-10 ml and used to evenly coat, by stirring, 10 g of unactivated Florisil contained in a small beaker. Stirring was maintained to give a dry, free-flowing, fat-coated powder.

This was then poured onto a 1-inch layer of unactivated Florisil in an 18-mm diameter column and eluted with 70 ml of 10% water in acetonitrile; the eluate was collected in a 1-liter separating funnel containing 100 ml of hexane.

From this point the procedures were the same as described in references (*6*) and (*7*), except that only one 200-ml elution at 5 ml/minute with 8% ether in hexane was used to remove all organochlorine pesticides, including dieldrin, from the final activated Florisil cleanup column used by Mills *et al.* (*7*). The removal of dieldrin with a single elution, however, would not have been possible if the Florisil had been made too active by prolonged heating.

Eluates were concentrated to about 0.5 ml and then transferred to glass-stoppered tubes, using hexane, to give a final volume of 2.0 ml. Aliquots from this solution were analyzed on a Varian Aerograph Model 1200 chromatograph equipped with a 250 mc tritium electron capture detector.

Operating conditions were:

| | | |
|---|---|---|
| Column: | Pyrex glass, 5′ x ⅛″, packed with an equal mixture of 10% DC-200 and 15% QF-1 on individually coated 80/100 mesh Gas Chrom Q. A glass liner was used in the injection port. | |
| Temperatures: | Oven | 180° C |
| | Detector foil | 185° C |
| | Inlet | 210° C |
| Carrier gas: | Nitrogen at 35 cc per minute | |

Injection volumes were held between 2 and 5 $\mu$l by sample dilution where necessary. The amounts of pesticides injected were kept within the linear range of the detector.

A hexane solution containing lindane, aldrin, dieldrin, DDD, DDE, and DDT, each at 0.1 ng/$\mu$l, was used as a standard. HCB (hexachlorobenzene) and BHC standard solutions were also used at 0.5 ng/$\mu$l. Injections of these standards were interspersed with samples during chromatography to provide peak height calibration graphs for quantitation.

All samples were chromatographed on a second column, packed with 12% QF-1 on Gas Chrom Q, to provide qualitative, and a small degree of quantitative, confirmation.

Thin layer chromatography with $AgNO_3$-UV visualization, as described by Abbott *et al.* (*2*), was also used to confirm about one-half of the samples. Additional confirmation of HCB was carried out on four samples by scraping the developed and UV-exposed HCB spot from the plate, extracting the alumina with hexane, and injecting the concentrated extract onto the first column.

Human milk samples spiked with chlorinated hydrocarbon pesticides to levels between 0.2 and 0.4 ppm gave the following recoveries when carried through the full analytical procedure: HCB and lindane—73-77%; aldrin, *p,p'*-DDD, *p,p'*-DDE, and *p,p'*-DDT—80-90%; and dieldrin—83%. The data presented in this report do not include recovery corrections. The lower limit of sensitivity was 0.001 ppm for 50 g of whole milk.

## *Results*

Total DDT shown in the results is the sum, without molecular weight adjustment, of the DDE, DDD, and DDT found.

As stated, the collection of samples occurred in two parts, separated by a period of 7 months. All of the 13 rural samples in the first collection were from one fruit-growing district, whereas the 26 rural samples in the second collection were from 10 other disparate rural areas. The directions given to obtain a representative milk sample from the donors also varied slightly between the two collections.

Table 2 shows the combined results in order to present the information in a unified form. Table 3 presents for total DDT and HCB only, the separate residue levels from the two surveys.

TABLE 2.—*Percent fat and organochlorine residues in milk from 67 human donors, Victoria, Australia, 1970*

| Compound | Number of Samples with Detectable Residues | Arithmetic Mean | Range | Geometric Mean | SD | SE |
|---|---|---|---|---|---|---|
| **PERCENT FAT IN WHOLE MILK** | | | | | | |
| Rural | 36 | 3.7 | 1.0-5.6 | — | 1.24 | 0.21 |
| Urban | 26 | 4.2 | 2.5-7.2 | — | 1.18 | 0.23 |
| Total | [1]62 | 3.95 | 1.0-7.2 | — | 1.25 | 0.16 |
| **ORGANOCHLORINE RESIDUES IN WHOLE MILK (PPM)** | | | | | | |
| **HCB** | | | | | | |
| Rural | 39 | 0.042 | 0.005-0.17 | 0.031 | 0.033 | 0.005 |
| Urban | 28 | 0.063 | 0.002-0.33 | 0.040 | 0.065 | 0.012 |
| Total | 67 | 0.051 | 0.002-0.33 | 0.035 | 0.050 | 0.006 |
| **Dieldrin** | | | | | | |
| Rural | 14 | 0.008 | 0.002-0.029 | — | — | — |
| Urban | 15 | 0.004 | 0.001-0.014 | — | — | — |
| Total | 29 | 0.006 | 0.001-0.029 | — | — | — |
| **DDE** | | | | | | |
| Rural | 39 | 0.100 | 0.022-0.45 | — | 0.088 | 0.012 |
| Urban | 28 | 0.112 | 0.012-0.29 | — | 0.070 | 0.013 |
| Total | 67 | 0.105 | 0.012-0.45 | — | 0.081 | 0.010 |
| **DDD** | | | | | | |
| Rural | 4 | 0.008 | 0.006-0.014 | — | — | — |
| Urban | 8 | 0.006 | 0.003-0.010 | — | — | — |
| Total | 12 | 0.007 | 0.003-0.014 | — | — | — |
| **DDT** | | | | | | |
| Rural | 39 | 0.038 | 0.007-0.16 | — | 0.033 | 0.005 |
| Urban | 28 | 0.034 | 0.007-0.12 | — | 0.022 | 0.004 |
| Total | 67 | 0.036 | 0.007-0.16 | — | 0.029 | 0.004 |
| **Total DDT** | | | | | | |
| Rural | 39 | 0.139 | 0.033-0.58 | 0.109 | 0.119 | 0.019 |
| Urban | 28 | 0.145 | 0.015-0.40 | 0.118 | 0.089 | 0.017 |
| Total | 67 | 0.141 | 0.015-0.58 | 0.112 | 0.107 | 0.013 |
| **Total DDT (Fat Basis)** | | | | | | |
| Rural | 36 | 4.63 | 0.81-25.35 | 3.22 | 5.21 | 0.87 |
| Urban | 26 | 3.73 | 1.11- 6.88 | 3.29 | 1.78 | 0.35 |
| Total | [1]62 | 4.25 | 0.81-25.35 | 3.25 | 4.16 | 0.53 |

[1] Insufficient sample in five cases for a fat determination.

TABLE 3.—*Total DDT and HCB residues in human milk from rural and urban donors by survey*

| Sample Group | Residues in PPM | | | | | |
|---|---|---|---|---|---|---|
| | Total DDT | | | HCB | | |
| | Arithmetic Mean | Range | Geometric Mean | Arithmetic Mean | Range | Geometric Mean |
| **APRIL 1970** | | | | | | |
| Rural (13 samples) | 0.208 | 0.045-0.58 | 0.145 | 0.039 | 0.010-0.080 | 0.031 |
| Urban (10 samples) | 0.142 | 0.015-0.40 | 0.105 | 0.040 | 0.002-0.090 | 0.025 |
| **DECEMBER 1970** | | | | | | |
| Rural (26 samples) | 0.104 | 0.033-0.20 | 0.095 | 0.043 | 0.005-0.17 | 0.031 |
| Urban (18 samples) | 0.147 | 0.051-0.31 | 0.125 | 0.076 | 0.016-0.33 | 0.052 |

Since the distribution of the levels is skew, geometric means are shown, and as the results for some pesticides cover a wide range, standard deviation and standard error of the mean have been included where considered appropriate.

Five samples were too meager to determine the fat content. The total DDT in each was 0.033, 0.015, 0.10, 0.072, and 0.058 ppm, all below the mean. However in the absence of fat determinations, it is difficult to assess the effect of their exclusion on the mean concentration of total DDT calculated on a fat basis.

Forty-three donors supplied the age of their baby at the time of the survey; these ages ranged from 2 to 46 weeks.

## *Discussion*

All samples contained HCB. It is possible that HCB entered the food chain of Victorians from the improper channeling of HCB-treated seed wheat into the local poultry and stock food industries following a series of severe reductions in wheat acreage during the period of worldwide wheat over-production in the past decade.

All samples contained DDT and its first metabolite DDE, but only 12 had the second metabolite DDD. Total DDT ranged from 0.015 to 0.58 ppm, with a mean of 0.141 ppm. These results may be considered in respect to other research findings. Egan *et al.* (*5*) reported total DDT in the range of 0.075 to 0.170 ppm with a mean of 0.126 ppm for 19 human milks in England. Curley and Kimbrough (*4*) determined total DDT in the milk of five U.S. women at three stages during a period of from 3 to 96 days postpartum. Although the range was small, 0.05 to 0.15 ppm, two subjects showed an increase in levels, two a decrease, and one a steady state over this period.

In this present study total DDT in human milk, on a fat basis, ranged from 0.81 to 25.35 ppm, with a geometric mean of 3.25 ppm. The ratio of DDE to DDT based on arithmetic means was 2.7 for rural donors, 3.3 for urban, and 2.9 overall.

Abbott *et al.* (*1*), in a study in the United Kingdom on postmortem human fat from 91 female subjects over 3 years of age, found total DDT to range from 0.21 to 8.10 ppm, with a geometric mean of 2.2 ppm. For their 248 male and female postmortem samples grouped according to sex, age, and district, they noted a fairly constant ratio for the groupings of 1 part of DDT to 2.6 parts DDE.

Bick (*3*), in a survey in Victoria using biopsy specimens of human body fat collected from 23 adult males and 30 adult females, found for total DDT a geometric mean of 2.00 ppm for the males, 1.68 ppm for the females, and a combined range of 0.48 to 6.35 ppm. These figures are on a fresh-tissue basis; mention is made that the lipid content of biopsy specimens is variable.

In this study, the mean levels of total DDT in human milk exceeded 0.05 ppm, the limit for total DDT in cow's milk proposed by the FAO/WHO and the tolerance set by the U. S. Food and Drug Administration. These limits are based in part on the fact that DDT is now widespread in the biosphere and on the expectation that an individual will consume milk in his diet for a lifetime. They do not provide for residues resulting from the deliberate use of DDT on dairy farms.

The results reported here thus pose a difficult problem for those who are responsible for advising mothers on the feeding of their newborn babies.

*Acknowledgment*

We thank Miss Christine Hartshorne for her assistance in the chemical analysis and officers of the Maternal and Child Welfare Branch of the State Department of Health, Victoria, for obtaining the samples.

See Appendix for chemical names of compounds discussed in this paper.

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# *Organochlorine Pesticide Levels in Human Serum and Adipose Tissue, Utah—Fiscal Years 1967-71* [1]

Stephen L. Warnick


## ABSTRACT

*Organochlorine pesticide residue levels were determined in 1,417 serum and 103 adipose samples collected during fiscal years 1967-71 from residents of Utah; levels agreed closely with values reported for persons from other parts of the United States. The results supported previous evidence of no increase in pesticide storage in the general population since 1951 and a tendency towards decreased storage since 1966. Specific findings from the Utah samples included the following:*

*(1) Significantly higher organochlorine levels were found in samples from persons occupationally exposed to pesticides than in those from the general population.*

*(2) Significantly higher levels of DDE were found in serum samples from persons 21 years of age and older than in those from persons under 21.*

*(3) Although residue levels were higher in males than in females, the difference was not significant.*

*(4) Mean values of total DDT in adipose tissue for the years in which these samples were obtained were 9.0 ppm in 1968, 7.2 ppm in 1969, and 5.3 ppm in 1970, indicating a decrease in storage levels.*

*(5) Lastly, results from studies of the relation between residue levels in serum and adipose tissue, between levels in serum and food, and between serum and household dust, indicated no significant correlations. However, the latter two correlations closely approximated a significant relationship, and the results suggested that the respiratory route of exposure to pesticides may be as significant as dietary intake in maintaining an individual's body burden of pesticides.*


[1] From the Utah Community Pesticide Study, State of Utah Department of Social Services, Division of Health, 44 Medical Drive, Salt Lake City, Utah 84113.

## *Introduction*

A chief concern regarding pesticides is the relationship between pesticide residues in human tissues and human health. Although current evidence indicates that present levels of pesticides in man's environment, food, and body are not adversely affecting human health, it is prudent to ascertain the body burden of pesticides. Numerous studies on pesticide levels in people have been reported (*1,3,5-8*), including two recently completed studies in Arizona (*2*) and Idaho (*4*).

Utah is one of 14 States under contract with the Federal Environmental Protection Agency to investigate the effect of pesticides on human health. One aspect of these studies is to determine levels of pesticides in the environment and human population of each project State. Since the projects are widely scattered throughout the contiguous United States and Hawaii, pooling results from these studies provides up-to-date representative information for the whole country.

This paper reports the results of 5 years' analyses for the presence of organochlorine pesticides in serum and adipose tissue samples from Utah residents. Residue levels are presented according to sex, age, race, and exposure of residents; method of sample analysis; and year of sampling. Results of studies correlating pesticide levels between serum and adipose tissue, between serum and food, and between serum and house dust are also reported. The discussion in this paper is limited to residues of *p,p'*-DDT, *p,p'*-DDE, total DDT (including

DDT, DDE, and DDD), and dieldrin, although several other residues were present in both serum and adipose tissue samples.

### *Sampling Methods and Analytical Procedures*

A total of 1,417 blood samples (fresh serum rather than whole blood) and 103 adipose tissue samples from the population of Utah were collected and analyzed for pesticide residues during the 5-year period, fiscal years 1967-71. The blood samples included 970 from the general population and 447 from persons occupationally exposed to pesticides.

Sample extraction, cleanup, and analyses were performed according to methods prescribed for the Community Pesticide Studies Laboratories. These included the Radomski (*21*) and the Mills, Onley, and Gaither (*22*) methods for analyzing adipose tissue; the Dale, Curley, and Cueto (*23*) method for blood; and modifications of the Mills method for adipose and the Dale method for serum as described in the "Manual of Analytical Methods" (*9*), prepared by the Primate Research Laboratories, Environmental Protection Agency, Perrine, Fla. The Perrine Laboratory also provided the pesticide standards used in this study and carried out a quality control program in which the Utah Laboratory participated. The MicroTek 220 gas chromatograph equipped with a $Ni^{63}$ detector was used for identifying pesticides, and a two-column gas chromatographic system was used routinely for confirmation. Recovery studies have shown that, for the pesticides reported, recovery is routinely greater than 90%.

### *Results*

Table 1 presents values from the literature for *p,p'*-DDT, *p,p'*-DDE, DDT + DDE, and dieldrin levels in people from various areas of the United States for comparison with levels in the general population of Utah. Residue levels in Utah residents compared closely with results from other areas of the country despite considerable differences in quantities of pesticides used.

Table 2 is a summary of organochlorine pesticide residue levels in blood of Utah residents according to sex, age, race, and exposure; method of analysis; and year of sampling. Table 3 presents organochlorine residue levels in adipose tissue, collected at autopsy from Utah residents who died in accidents; these data are given according to the residents' sex, age, race, and year of sampling.

TABLE 2.—*Average organochlorine pesticide residue levels in human serum, Utah—fiscal years 1967-71*

| | No. of Samples | Residues in ppb | | | |
|---|---|---|---|---|---|
| | | *p,p'*-DDE | *p,p'*-DDT | Total DDT[1] | Dieldrin |
| Total | 1,417 | 19.8 | 6.2 | 28.3 | 1.8 |
| Sex | | | | | |
| Male | 1,003 | 21.9 | 6.9 | 31.5 | 2.1 |
| Female | 414 | 14.6 | 4.3 | 20.5 | 0.9 |
| Year | | | | | |
| FY 1967 | 72 | 19.5 | 9.8 | 32.8 | 4.5 |
| FY 1968 | 237 | 15.4 | 7.2 | 24.7 | 2.1 |
| FY 1969 | 267 | 20.8 | 7.9 | 31.2 | 1.6 |
| FY 1970 | 439 | 18.7 | 4.3 | 25.1 | 1.6 |
| FY 1971 | 402 | 22.9 | 5.7 | 31.2 | 1.4 |
| Method of Analysis | | | | | |
| Method 1 (Single Extract) | 172 | 15.2 | 8.4 | 26.1 | 3.4 |
| Method 2 (Triple Extract) | 843 | 19.3 | 5.9 | 27.4 | 1.6 |
| Method 3 (2-hour Roto-rack Ext.) | 402 | 22.9 | 5.7 | 31.2 | 1.4 |
| Exposure Group | | | | | |
| Exposed Workers | 447 | 24.7 | 11.1 | 38.9 | 3.7 |
| General Population | 970 | 17.6 | 3.8 | 23.4 | 0.9 |
| Age | | | | | |
| < 21 | 202 | 13.4 | 3.6 | 18.5 | 0.6 |
| ≥ 21 | 1,215 | 20.9 | 6.6 | 29.9 | 2.0 |
| Race | | | | | |
| Caucasian | 1,347 | 19.8 | 6.0 | 28.1 | 1.8 |
| Negro | 4 | 14.3 | 4.8 | 20.8 | 0.8 |
| Oriental | 22 | 35.6 | 18.6 | 58.4 | 1.0 |
| Indian | 43 | 14.0 | 4.4 | 20.1 | 0.5 |
| Mexican | 1 | 16.0 | 3.0 | 21.0 | 1.0 |

[1] Total DDT = DDT + 1.114 (DDE + DDD), formula used to adjust for differences in molecular weight.

TABLE 1.—*Mean organochlorine pesticide concentrations in human blood and adipose tissue from Utah and levels reported for other areas of the United States*

| Compound | Utah | | Chicago[1] | | Arizona[2] | | Florida[3] | | Idaho[4] | | Utah[5] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Blood (ppb) N=970 | Adipose (ppm) N=103 | Blood (ppb) | Adipose (ppm) N=959 | Blood (ppb) | Adipose (ppm) N=70 | Blood (ppb) N=119 | Adipose (ppm) N=159 | Blood (ppb) N=100 | Adipose (ppm) | Blood (ppb) | Adipose (ppm) N=89 |
| *p,p'*-DDT | 3.8 | 1.5 | | 2.4 | | 1.5 | 7.0 | 4.3 | 4.7 | | 4.7 | 1.3 |
| *p,p'*-DDE | 17.6 | 5.0 | | 6.4 | | 4.6 | 11.3 | 7.0 | 22.0 | | 22.5 | 4.5 |
| DDT + DDE | 21.4 | 6.5 | | 8.8 | | 6.1 | | 11.3 | 26.7 | | 27.2 | 5.8 |
| DIELDRIN | 0.90 | 0.17 | | 0.14 (N=221) | | 0.14 | | | 0.5 | | | 0.04 |

[1] Hoffman *et al.*, 1967.
[2] Morgan and Roan, 1970.
[3] Davies *et al.*, 1968.
[4] Watson *et al.*, 1970.
[5] Casarett *et al.*, 1968.

TABLE 3.—*Average organochlorine pesticide residue levels in human adipose tissue, Utah—fiscal years 1967-71*

| | No. of Samples | Residues in ppb | | | |
|---|---|---|---|---|---|
| | | *p,p'*-DDE | *p,p'*-DDT | Total DDT[1] | Dieldrin |
| Total | 103 | 5.03 | 1.53 | 7.31 | 0.17 |
| Sex | | | | | |
| Male | 71 | 5.36 | 1.68 | 7.85 | 0.19 |
| Female | 32 | 4.31 | 1.20 | 6.10 | 0.14 |
| Year | | | | | |
| FY 1968 | 48 | 5.95 | 2.13 | 9.01 | 0.20 |
| FY 1969 | 15 | 4.81 | 1.51 | 7.15 | 0.15 |
| FY 1970 | 40 | 4.02 | 0.83 | 5.33 | 0.15 |
| FY 1971 | No fat samples analyzed | | | | |
| Age | | | | | |
| < 21 | 15 | 4.11 | 1.25 | 5.97 | 0.09 |
| ≥ 21 | 88 | 5.19 | 1.58 | 7.54 | 0.19 |
| Race | | | | | |
| Caucasian | 96 | 4.75 | 1.32 | 6.76 | 0.16 |
| Negro | 4 | 7.90 | 3.70 | 12.70 | 0.20 |
| Oriental | 1 | 14.40 | 11.50 | 29.60 | 0.80 |
| Indian | 1 | 4.80 | 1.50 | 7.10 | 0.30 |
| Mexican | 1 | 11.40 | 3.10 | 16.40 | 0.30 |

[1]Total DDT = DDT + 1.114 (DDE + DDD), formula used to adjust for differences in molecular weight.

## *Discussion*

There is no evidence of increased storage of organochlorine pesticides in the general population since 1951 (*13*), and, further, this study and others show a tendency toward decreasing levels since 1966. The fact that there has not been progression in storage can probably be attributed to regulations that have maintained low dietary residues.

The question of changes in pesticide levels with time is interesting but complicated by the need for standardized analytical methodology. Improved methods of analysis the past few years have offset the very subtle changes that may have taken place in tissue stores as related to changing patterns of pesticide usage.

In comparing total DDT in the blood of Utah people as related to sex, the overall average for males was 31.5 ppb and 20.5 ppb for females. Total DDT in adipose was 7.8 ppm for males and 6.1 ppm for females. In both cases, the levels in males were higher, but the difference was not found to be statistically significant.

In comparing total DDT in the blood as related to age, levels in persons 21 years of age and older averaged 29.9 ppb, and levels in those under 21 years averaged 18.5 ppb. In adipose tissue persons 21 years of age and older had average levels of 7.5 ppm, while those under 21 years had 6.0 ppm. In both cases the levels of total DDT in people over 21 years were higher but not significantly so. Of the individual compounds, only for levels of serum DDE was the difference according to age significant.

In comparing total DDT in the blood as related to exposure, results showed that the general population had an average level of 23.4 ppb, while a group of occupationally exposed workers averaged 38.9 ppb; this difference is significant at ($P < 0.05\%$). Adipose tissue was obtained only from the general population; the average level for total DDT was 7.3 ppm.

In comparing total DDT in the blood by method of analysis, residues determined using the single hexane extraction method averaged 26.1 ppb; the triple hexane extraction method, 27.4 ppb; and the 2-hour roto-rack hexane extraction method, 31.2 ppb. The last two methods significantly increased DDE recovery, but not DDT. These more efficient analytical methods may have offset a decline in storage levels of DDE in blood during years 1969, 1970, and 1971. There were some changes in the method for adipose analysis, but the changes did not affect pesticide recovery significantly.

Comparison of total DDT found in the blood by year, is difficult due to changes in analytical methodology, but levels for 1967, 1969, and 1971 were higher than levels in 1968 and 1970. An interesting trend was noted in the adipose samples which averaged 9.0 ppm in 1968, 7.1 ppm in 1969, and 5.3 ppm in 1970. This decrease may have been related to a 75% reduction in the use of DDT in Utah during this same period. A budget cut in fiscal year 1971 prevented collection of adipose tissue this year, so it was not determined if the downward trend continued.

An insufficient number of samples made a comparison of DDT in the blood and adipose as related to race invalid, except perhaps in the case of American Indians. A total of 43 blood samples were obtained from American Indians; these averaged 20.1 ppb compared to 28.1 ppb for Caucasians, perhaps reflecting less exposure for the Indians.

Although many studies have investigated the mechanics of DDT storage and metabolism, even after two decades the process is not completely understood. There does appear to be a direct relationship between the daily intake of DDT and levels in the fat achieved at equilibrium. Hayes (*14*) reached this conclusion by feeding DDT to human volunteers for 18 months and showing that even when doses were 200 times as much as found in the daily diet, DDT and DDE concentration in the fat leveled off in about a year. Other studies have supported his finding.

When DDT is ingested, carbon-14 studies (*15*) have shown that a good portion is not absorbed, but excreted directly in the feces. As much as 19% is also excreted

in the feces and urine as DDA. The remainder is in equilibrium between storage in the fat and circulation in the blood where it is gradually metabolized and excreted.

Recent studies have shown that pesticide storage is affected by other pesticides, certain drugs, and diet deficiencies (*16-19*). A study in Arizona (*20*) in which human volunteers were given DDT showed that DDT ingestion does not markedly increase DDE storage, indicating that the body burden of DDE is ingested as DDE. Only about 8% of the stored DDE came from the ingested DDT.

There was no attempt in this paper to relate pesticide levels to pathology; but other studies (*1,2,10-12*) have shown no correlation between levels similar to those found in Utah residents and abnormalities in human health. On this basis, it can be assumed that present levels of organochlorine pesticides in Utah people are not a threat to the health of the community.

## CORRELATION STUDIES

A study was done on 40 people supplying both adipose tissue and serum samples to determine if a significant correlation existed between pesticide levels in adipose and serum. The correlation coefficients (r) were 0.22 for *p,p′*-DDT and 0.06 for *p,p′*-DDE. To be significant at $P < 5\%$ for 40 samples, the correlation coefficient must be $r = 0.32$, thus no statistically significant relationship was found between levels in the two types of samples.

Another part of the research by the Utah Community Pesticide Study is to determine environmental pesticide levels in food, water, air, house dust, soil, wildlife, etc. To accomplish this, total diet food samples and vacuum cleaner dust samples are collected from selected homes and analyzed for pesticide residues. A study was done to see if DDT levels in the serum correlated with either DDT levels in food or DDT levels in house dust. Ten homes representing the minimally exposed general population were chosen. Blood samples were also collected from the male head-of-household and analyzed for pesticides. The following correlation coefficients were then determined for total DDT residues between serum and food, $r = 0.41$ and between serum and house dust, $r = 0.47$. To be significant at $P < 5\%$ for a sample of 10, the correlation coefficient would have to be $r = 0.52$, thus neither of these relationships was statistically significant. It is interesting to note, however, that the correlation is greater between serum and house dust than between serum and food. This is reasonable based on the fact that the mean level of total DDT in house dust was 1000 times greater than in food (5120 ppb house dust; 6.13 ppb food). This does indicate that the respiratory route of exposure may be as significant as diet in maintaining a person's body burden of pesticides. Additional samples are being collected and analyzed in an attempt to confirm this theory.


### *Acknowledgment*

Pesticide analyses were performed with the assistance of Lynn Thomas, and data analyses were done by Tom Whaley.


See Appendix for chemical names of compounds discussed in this paper.


The Utah Community Studies Pesticides Project was supported under contract by the Division of Pesticide Community Studies, Office of Pesticides Programs, Environmental Protection Agency through the Utah State Division of Health.


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# RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

## *Mirex and DDT Residues in Wildlife and Miscellaneous Samples in Mississippi—1970* [1]

Karl P. Baetcke, Jimmie D. Cain, and William E. Poe

ABSTRACT

*Samples of wildlife and a few miscellaneous samples, such as beef, were collected in Mississippi in 1970 and analyzed for the presence of mirex and DDT and its analogs. Levels of mirex residues were found to range from 0 ppm to a high of about 104 ppm; residues of DDT and its metabolites (DDTR = DDT + DDE + DDD) were found to range from<0.001 ppm to 126 ppm. Comparisons of the amounts of the two pesticides found in individual samples showed that mirex residues often exceeded DDT residues. Collections of wildlife were begun in the spring of 1970, 1 year after mirex had been applied by aerial application in the primary study area. The high levels of mirex residues found in some of these samples 1 year after treatment indicate that mirex can be considered a persistent pesticide.*

### *Introduction*

The insecticide mirex has been used widely in Mississippi and other parts of the Southeast for the control of the imported fire ant (*Solenopsis saevissima*).

Mirex was first used in Mississippi in 1962. It has since been employed by farmers in many parts of the State for local fire ant control and, in some instances, in county-wide programs involving aerial application. For example, in 1962, 40,000 acres in Washington County in the Delta were aerially treated in an apparently successful attempt to eradicate a fire ant infestation. In 1965, 1966, and 1967, an aerial application program was conducted in portions of eight counties located in northeastern Mississippi. In 1969, portions of Oktibbeha, Noxubee, and Lowndes Counties were treated with mirex by aerial application; Oktibbeha and Noxubee Counties each received two applications and Lowndes County received three applications. In this instance, 1.25 lb of bait containing 0.3% mirex was applied per acre. These counties, located in the hill section of east central Mississippi, were thought to be areas in which wildlife might have accumulated mirex as a result of recent exposure.

This report presents data on mirex residues in deer, birds, fish, arthropods, beef, cows' milk, bird eggs, earthworms, silage, and fescue from these counties. The samples were also analyzed for DDT and its analogs in order to make possible some general comparisons between residues representing a pesticide (mirex) which has been employed recently primarily in local situations and one (DDT) which has had long-term widespread usage. A few additional samples were collected in the Delta area of Mississippi where no recent applications of mirex had been made, and results of analysis for mirex residues in these samples are also discussed in this report.

### *Sampling*

The species selected as samples for this investigation were chosen to represent as wide a variety as possible of the larger species in the food chain. The following species were collected for analysis:

| | |
|---|---|
| Deer | *Odocoileus virginianus* (Zimmerman) |
| Birds | |
| chicken | *Gallus gallus* |
| bobwhite quail | *Colinus virginianus* (Linnaeus) |
| brown thrasher | *Toxostoma rufum* (Linnaeus) |
| blue jay | *Cyanocitta cristata* (Linnaeus) |
| meadow lark | *Sturnella magna* (Linnaeus) |
| turkey | *Meleagris gallopavo* (Linnaeus) |
| eastern kingbird | *Tyrannus tyrannus* (Linnaeus) |
| robin | *Turdus migratorius* (Linnaeus) |
| barred owl | *Strix varia* (Barton) |

[1] From the Mississippi Community Study on Pesticides, Department of Biochemistry, Mississippi State University, State College, Miss. 39762.

| | |
|---|---|
| Fish | |
| channel catfish | *Ictalurus punctatus* (Rafinesque) |
| green sunfish (bream) | *Lepomus cyanellus* (Rafinesque) |
| Arthropods | |
| crickets | Orthoptera:Gryllidae |
| spiders | Arachnida |
| chinch bugs | Hemiptera:Lygaeidae |
| pill bugs | Isopoda |
| beetles | Coleoptera:Carabidae, Elateridae, Coccinellidae, Chrysomelidae |
| walking sticks | Orthoptera:Phasmidae |
| praying mantis | Orthoptera:Mantidae |
| stink bugs | Hemiptera:Pentatomidae |
| katydid | Orthoptera:Tettigoniidae |
| grasshoppers | Orthoptera:Locustidae |
| Miscellaneous | |
| cattle egret eggs | *Bubulcus ibis* (Linnaeus) |
| little blue heron eggs | *Florida caerulea* (Linnaeus) |
| cows' milk | |
| earthworm | *Lumbricus terrestris* (Linnaeus) |
| beef | |
| silage | |
| fescue | *Festuca* sp. |

Deer samples were obtained from freezer locker plants and from hunters in the Delta area in and around Greenville, Mississippi, and in east central Mississippi near Oktibbeha, Noxubee, and Lowndes Counties (hereafter referred to as the hill area). The bird samples except for two robins collected in the Delta were from the hill area around Starkville and the Noxubee Wildlife Refuge; all arthropods, fish, and miscellaneous samples were from the hill area (Oktibbeha and Lowndes Counties). All samples from the hill area were obtained from locations which had been subjected to mirex applications.

### *Analytical Procedures*

The sampled species, although differing widely in type, did not present any unusual problems in extraction or cleanup for residue analysis. The procedures chosen for extraction and cleanup of mirex, the pesticide of specific interest in this study, as well as DDT were already well established although recovery rates for mirex were not available. Recovery rates for both mirex and DDT and its analogs were determined for this study. Electron capture gas-liquid chromatography was utilized in the determinative step. Thin layer chromatography and infrared spectroscopy were utilized as confirmatory procedures in selected samples. Fish and birds were dissected and the liver, adipose, and brain tissues were analyzed separately by the procedure described in the Pesticide Analytical Manual, Vol. III (*1*); however, adipose tissue was not obtained from all avian species because of an apparent depletion of fat reserves.

Only adipose tissue was selected from beef and deer for analysis, using the same procedures as that for fish and bird tissue analysis. However, because of the variation in the state of the deer samples which included fresh tissues, dehydrated tissues, and, in extreme cases, partially decomposed tissues, meaningful comparisons of residue values based on fresh weights were not possible. Therefore, in order to make the deer fat samples more comparable, the samples were ground in a Duall tissue grinder with petroleum ether (b.p. 30-60° C), the ether evaporated on a 60° C water bath, and sampling for residue analysis made on the resulting petroleum ether soluble lipids according to Enos *et al.* (*1*).

Residues in cows' milk were determined on a fat basis utilizing the procedure described in the Pesticide Analytical Manual, Vol. I (*2*) for the extraction of fat. Cleanup of the milk fat prior to GLC analysis was accomplished by the procedure of Langlois, Stemp, and Liska (*3*) with the following modification: Instead of incorporating fluid milk into the top Florisil layer, 1 g or less of extracted butterfat contaned in about 25 ml of 30-60° C petroleum ether was incorporated into Florisil (deactivated with 5% water) to form the top layer. This modification extends the usefulness of this cleanup method making it applicable to a wide variety of plant and animal tissue extracts. Extraction of residues from silage and fescue samples was handled essentially as described by Mills, Onley, and Gaither (*4*). This was followed by cleanup as previously described for milk fat.

Extraction and cleanup of cattle egret and little blue heron eggs were accomplished according to Cummings *et al.* (*5*); no problems were encountered during subsequent gas chromatography. Arthropods and earthworms were composited by maceration in a Duall tissue grinder, and the micromethod of Enos *et al.* (*1*) was used for the extraction, cleanup, and residue determination on the composite.

Primary identification and quantification of the pesticides were accomplished on a MicroTek NT-220 gas chromatograph. Two columns having different resolution characteristics were utilized on every sample. Instrument parameters were as follows:

| | |
|---|---|
| Columns: | (A) Borosilicate glass, 6′ x ¼″, packed with 1.5% OV-17, 1.95% QF-1 on 80/100 mesh Supelcoport |
| | (B) Borosilicate glass, 6′ x ¼″, packed with 4% SE-30, 6% QF-1 on 80/100 mesh Suplecoport |
| Detector: | Electron capture, having 130 mc tritium ionizing source |

| | | |
|---|---|---|
| Temperatures: | Injector | 235° C |
| | Column | 195° C |
| | Detector | 210° C |
| Carrier gas: | Prepurified nitrogen flowing at 90 ml/min (Column A) and 60 ml/min (Column B) | |

RECOVERY RATES

To establish recovery rates, adipose, liver, and brain tissues collected from chickens were spiked with known amounts of *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDE, and mirex, and the tissues were then analyzed for these residues utilizing the procedures described above. Recoveries on each tissue were based on three unspiked samples and two levels of fortification with DDTR (DDT and its analogs) and mirex, each consisting of three replicates. The first level consisted of 0.21 ppm DDTR (0.10 ppm *p,p'*-DDE + 0.10 ppm *p,p'*-DDT + 0.01 ppm *o,p'*-DDT) and 0.10 ppm mirex; the second level consisted of 21.00 ppm DDTR (10.00 ppm *p,p'*-DDE + 10 ppm *p,p'*-DDT + 1.00 ppm *o,p'*-DDT) and 10.00 ppm mirex. Percent recoveries at the first level averaged 110%, 88%, and 98% for DDTR and 71%, 81%, and 110% for mirex in adipose, liver, and brain tissue, respectively. At the second level, recoveries were 93%, 85%, and 102% for DDTR and 82%, 91%, and 102% for mirex in adipose, liver, and brain tissue, respectively.

Efficiency of the analytical technique utilized on arthropods was determined by grinding 10 crickets and dividing the material into four 500 mg samples consisting of three spiked samples and one blank. The spike consisted of 1.0 ppm *p,p'*-DDT, 1.0 ppm *p,p'*-DDE, 0.1 ppm *o,p'*-DDT, and 1.0 ppm mirex. Based on one level of fortification and three replicates, percent recovery averaged 86% for DDTR and 92% for mirex. None of the data presented herein were corrected on the basis of recovery rates.

Confirmation of the presence of mirex was made by thin layer chromatography of six samples (two brown thrashers, two bluejays, one channel catfish, and one robin), on Brinkmann-Silica Gel-G plates and developed with n-heptane solvent. Retention values for the mirex standard and for the mirex extracted from samples both averaged .75, thus confirming the identification of the extracted compound as mirex. Further confirmation of the presence of mirex was obtained from infrared spectra of two samples (the channel catfish and one blue jay); however, additional infrared spectra could not be obtained due to insufficient quantities of mirex in the remaining four samples.

Confirmation of DDT and its analogs was accomplished by extraction p-values in some similar wildlife samplings carried out prior to the experiments relating to this study. Many confirmations by this technique have been made in the past, and to date, polychlorinated biphenyls have not been found to be present in quantities sufficient to interfere with DDT calculations. It is true that PCB's, when present at high enough concentrations, interfere with identification of *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, and others. However, PCB's, notably Aroclor 1254 and Aroclor 1248, also exhibit tell-tale electron capture responses in regions of the chromatogram both earlier and later than that occupied by DDT and analogs. None of these patterns were observed in any samples in this study. This fact does not, of course, preclude the presence or absence of PCB's. It does show, however, that they were not present in high enough concentrations to interfere with the identification and quantitation of DDT and its analogs under the conditions of these experiments.

## *Results and Discussion*

The results of the analyses for mirex residues are given in Tables 1-4. Each table also shows the amount of DDTR (the sum of *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD) found in each sample analyzed. Mirex residues were found to range from 0 ppm to a high of about 104 ppm; DDT and its metabolites (DDTR = DDT + DDE + DDD) were found to range from <0.001 ppm to 126 ppm.

By analyzing for DDT residues, in addition to mirex residues, it was possible to make some general comparisons between residues representing a pesticide which has been employed primarily in local situations very recently (mirex) and one which has had long-term widespread usage (DDT). Data are presented on individual samples in the tables in order that more com-

TABLE 1.—*Mirex and DDT residues in adipose tissue of deer collected in Noxubee, Oktibbeha, and Monroe Counties, Mississippi—1970*

| Deer Sample Number | Residues in ppm | | | | | |
|---|---|---|---|---|---|---|
| | *p,p'*-DDE | *p,p'*-DDD | *o,p'*-DDT | *p,p'*-DDT | DDTR | Mirex |
| 1 | 0.015 | 0.010 | — | 0.096 | 0.121 | — |
| 2 | 0.015 | 0.010 | — | 0.107 | 0.132 | — |
| 3 | 0.025 | 0.014 | 0.011 | 0.059 | 0.109 | 0.091 |
| 4 | 0.035 | 0.029 | — | 0.178 | 0.242 | 0.175 |
| 5 | 0.023 | 0.013 | 0.007 | 0.102 | 0.145 | — |
| 6 | — | 0.014 | — | 0.057 | 0.070 | 0.283 |
| 7 | 0.033 | 0.014 | 0.007 | 0.094 | 0.148 | — |
| 8 | 0.105 | 0.316 | — | 1.290 | 1.711 | — |
| 9 | 0.038 | 0.015 | — | 0.083 | 0.135 | — |
| 10 | 0.059 | 0.029 | — | 0.359 | 0.447 | — |
| 11 | 0.055 | 0.022 | — | 0.188 | 0.265 | — |
| 12 | 0.051 | 0.034 | — | 0.128 | 0.213 | 0.305 |
| 13 | 0.022 | 0.016 | 0.007 | 0.101 | 0.146 | 0.064 |
| 14 | 0.006 | 0.008 | — | 0.063 | 0.077 | — |
| 15 | 0.114 | 0.035 | — | 0.405 | 0.554 | — |
| 16 | 0.098 | 0.074 | — | 0.428 | 0.600 | — |
| 17 | 0.025 | 0.007 | 0.009 | 0.080 | 0.121 | 0.045 |
| 18 | 0.032 | 0.024 | 0.009 | 0.112 | 0.177 | 0.120 |
| 19 | 0.036 | 0.025 | 0.012 | 0.187 | 0.270 | — |

NOTE: — indicates none detected; all results on lipid basis.

plete comparisons can be made between DDTR residues and mirex residues.

The results of the current investigation demonstrate widespread occurrence of mirex in wildlife in the treated area. Of 19 deer adipose samples from the hill area of Mississippi, 7 contained mirex (Table 1). Mirex was not found in any of 51 samples collected from deer in the Delta where mirex use had been sporadic and very localized. Data pertaining to the Delta deer samples are not presented in the tables since the main purpose of this report is to compare levels of mirex with levels of DDT, as well as to show to what extent mirex is present in samples from the treated area.

Of 42 individual birds representing 9 species analyzed for the presence of mirex, mirex was found present in one or more tissues of 41 birds (Tables 2a-2d). Mirex was not found in any tissue of one turkey (Tables 2a-2c). Of all fish from the hill area analyzed for mirex,

TABLE 2a.—*Mirex and DDT residues in liver tissue of fish and birds collected in Oktibbeha, Noxubee, and Lowndes Counties, Mississippi—1970*

| Specimen | Sample Number[1] | Residues in ppm | | | | | |
|---|---|---|---|---|---|---|---|
| | | *p,p'*-DDE | *p,p'*-DDD | *o,p'*-DDT | *p,p'*-DDT | DDTR | Mirex |
| Fish | 1 | 0.046 | 0.011 | T | 0.012 | 0.069 | 0.281 |
| Channel catfish | 2 | 0.004 | — | — | — | 0.004 | 0.023 |
| | 3(2) | 0.089 | 0.044 | 0.046 | 0.048 | 0.227 | 0.337 |
| | 4(2) | 0.121 | — | 0.052 | 0.024 | 0.197 | 0.674 |
| | 5 | 0.023 | 0.028 | 0.047 | 0.060 | 0.158 | — |
| | [2]6 | 0.054 | 0.063 | 0.061 | 0.068 | 0.246 | — |
| | [2]7 | 0.024 | 0.052 | 0.056 | 0.021 | 0.153 | — |
| Birds | | | | | | | |
| Chicken | 1 | 0.823 | 0.047 | 0.024 | 0.150 | 1.044 | 0.550 |
| Bobwhite quail | 1 | 0.404 | — | — | 0.006 | 0.410 | 0.013 |
| | 2 | 0.389 | 0.003 | 0.012 | 0.007 | 0.411 | 0.027 |
| | 3 | 0.101 | T | T | T | 0.101 | — |
| | 4 | 0.421 | T | T | T | 0.421 | — |
| | 5 | 0.400 | T | T | T | 0.400 | — |
| | 6 | 0.156 | T | T | T | 0.156 | 0.014 |
| | 7 | 0.281 | T | T | 0.018 | 0.299 | 0.052 |
| | 8 | 0.459 | T | 0.015 | T | 0.474 | 0.016 |
| | 9 | 0.270 | 0.005 | 0.012 | 0.017 | 0.304 | 0.077 |
| | 10 | 0.144 | 0.004 | — | 0.009 | 0.157 | — |
| | 11 | 0.487 | T | 0.016 | T | 0.503 | 0.031 |
| | 12 | 0.303 | T | T | T | 0.303 | 0.027 |
| | 13 | 0.057 | T | T | T | 0.057 | 0.026 |
| | 14 | 0.371 | T | T | T | 0.371 | 0.147 |
| | 15 | 0.021 | T | T | T | 0.021 | 0.034 |
| | 16 | 0.254 | — | — | — | 0.254 | 0.034 |
| | 17 | 0.194 | T | T | T | 0.194 | 0.209 |
| | 18 | 0.339 | T | — | T | 0.339 | 0.216 |
| | 19 | 0.161 | — | — | — | 0.161 | 0.050 |
| | 20 | 0.111 | — | — | — | 0.111 | 0.295 |
| Brown thrasher | 1 | 1.369 | — | 0.029 | 0.026 | 1.424 | 0.456 |
| | 2 | 1.519 | — | — | 0.118 | 1.637 | 1.811 |
| | 3 | 4.228 | — | 0.046 | 0.119 | 4.393 | 1.838 |
| | 4 | 1.725 | — | 0.015 | 0.045 | 1.785 | 1.242 |
| Blue jay | 1 | 0.499 | — | 0.013 | 0.046 | 0.558 | 1.434 |
| | 2 | 0.415 | — | — | — | 0.415 | 0.350 |
| | 3 | 0.514 | — | — | 0.023 | 0.537 | 1.506 |
| Meadow lark | 1 | 1.312 | 0.010 | 0.014 | 0.233 | 1.569 | 7.564 |
| | 2 | 1.348 | 0.007 | 0.011 | 0.095 | 1.461 | 3.744 |
| Turkey | 1 | 0.090 | — | — | T | 0.090 | 0.076 |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | | | | | | |
| | 5 | 1.130 | 0.010 | 0.010 | 0.026 | 1.176 | 0.206 |
| | 6 | 0.329 | T | T | 0.033 | 0.362 | 0.475 |
| Eastern kingbird | 1 | 5.462 | 0.077 | 0.154 | 0.308 | 6.001 | 0.131 |
| Robin | 1 | — | — | — | — | — | — |
| | 2 | 13.879 | 5.042 | 0.206 | 0.158 | 19.285 | 0.724 |
| | 3 | 13.332 | 4.220 | 0.174 | 0.255 | 17.951 | 0.298 |
| | 4 | 0.583 | 0.062 | 0.039 | 0.089 | 0.773 | 1.443 |
| | 5 | 1.683 | 0.151 | 0.044 | 0.086 | 1.964 | 0.694 |
| Barred owl | 1 | 4.046 | 0.012 | — | 0.052 | 4.110 | 4.072 |

NOTE: Blank = sample not analyzed; — indicates none detected; T = trace = <0.002 ppm mirex; all results on fresh-weight basis.
[1] Numbers in parentheses indicate composite of two or more fish or birds.
[2] Samples collected in the Delta.

4 of 5 channel catfish samples were found to contain the pesticide (Tables 2a, 2b, 2d) and 2 of 2 green sunfish (bream) samples were found to contain the pesticide (Table 2b). Of 25 individual and composite samples of arthropods analyzed for pesticides, 10 were found to contain mirex. It should be pointed out that all of the samples containing mirex, with the exception of two robins, were collected from the area that had been treated relatively recently with mirex.

Among the few miscellaneous samples collected, the significant findings were that mirex was present in the two milk samples and the three beef samples (adipose tissue) collected (Table 4). One milk fat sample contained 0.007 ppm of mirex and the other contained 0.016 ppm. The values for mirex in the three beef fat samples were 0.012, 0.113, and 0.042 ppm. The results of the analyses for mirex in beef fat and milk, in addition to results concerning the deer samples, suggest that this

TABLE 2b.—*Mirex and DDT residues in adipose tissue of fish and birds collected in Oktibbeha, Noxubee, and Lowndes Counties, Mississippi—1970*

| Specimen | Sample Number[1] | Residues in ppm | | | | | |
|---|---|---|---|---|---|---|---|
| | | *p,p'*-DDE | *p,p'*-DDD | *o,p'*-DDT | *p,p'*-DDT | DDTR | Mirex |
| Fish | | | | | | | |
| Green sunfish (Bream) | 1 | 0.086 | 0.010 | T | 0.016 | 0.112 | 0.138 |
| | 2 | 0.068 | 0.008 | 0.009 | 0.024 | 0.109 | 0.105 |
| Channel catfish | 1 | 0.579 | 0.088 | 0.013 | 0.087 | 0.767 | 11.252 |
| | 2 | 0.211 | 0.076 | 0.036 | 0.058 | 0.381 | 5.978 |
| | 3(2) | 1.170 | 0.399 | 0.112 | 0.559 | 2.240 | 3.760 |
| | 4(2) | 2.382 | 0.659 | 0.309 | 0.783 | 4.133 | 2.479 |
| | 5 | 1.953 | 2.421 | 1.371 | 2.189 | 7.934 | — |
| | [2]6 | 3.579 | 2.935 | 0.753 | 2.885 | 10.152 | — |
| | [2]7 | 1.968 | 2.021 | 1.296 | 2.402 | 7.687 | — |
| Birds | | | | | | | |
| Chicken | 1 | 0.067 | 0.004 | — | 0.030 | 0.101 | 0.087 |
| Bobwhite quail | 1 | 0.073 | — | — | — | 0.073 | 0.252 |
| | 2 | T | — | — | — | T | — |
| | 3 | 0.014 | — | — | — | 0.014 | 0.016 |
| | 4 | 0.141 | — | — | T | 0.141 | 0.072 |
| | 5 | 0.074 | T | T | 0.046 | 0.120 | 0.038 |
| | 6 | 0.063 | T | T | T | 0.063 | 0.036 |
| | 7 | 0.085 | — | — | — | 0.085 | 1.047 |
| | 8 | 0.050 | — | — | T | 0.050 | 0.410 |
| | 9 | 0.071 | — | — | — | 0.098 | 0.147 |
| | 10 | 0.017 | — | — | — | 0.017 | 0.177 |
| | 11 | 0.290 | T | T | 0.038 | 0.328 | T |
| | 12 | 0.908 | 0.015 | 0.023 | 0.032 | 0.987 | 3.148 |
| | 13 | 0.580 | 0.015 | 0.036 | 0.060 | 0.515 | 0.691 |
| | 14 | 0.511 | T | T | 0.863 | 1.374 | 0.843 |
| | 15 | 0.840 | 0.010 | — | 0.037 | 0.887 | 2.755 |
| | 16 | 0.291 | T | T | 0.040 | 0.331 | 0.292 |
| | 17 | 0.398 | 0.014 | T | 0.042 | 0.454 | 0.907 |
| | 18 | 0.763 | 0.024 | 0.043 | 0.071 | 0.901 | 1.610 |
| | 19 | 0.407 | T | T | 0.072 | 0.479 | 0.717 |
| | 20 | 0.758 | T | T | 0.092 | 0.850 | 1.843 |
| Brown thrasher | 1 | 17.732 | 0.261 | T | 1.390 | 19.122 | 53.563 |
| | 2 | 28.380 | 0.176 | 0.197 | 2.589 | 31.342 | 59.925 |
| | 3 | 60.086 | 0.337 | 0.167 | 4.677 | 65.267 | 25.432 |
| | 4 | 33.629 | T | T | 1.990 | 35.619 | 19.978 |
| Blue jay | 1 | 29.779 | T | T | 2.963 | 32.742 | 104.386 |
| | 2 | 8.388 | 0.077 | 0.153 | 0.481 | 9.029 | 5.104 |
| | 3 | 50.381 | T | T | 2.607 | 52.988 | 35.720 |
| Turkey | 1 | 0.889 | 0.036 | 0.025 | 0.593 | 1.543 | 1.614 |
| | 2 | 2.936 | 0.110 | 0.084 | 2.290 | 5.420 | 0.156 |
| | 3 | 0.091 | T | T | 0.074 | 0.165 | 0.014 |
| | 4 | 0.053 | 0.005 | T | 0.099 | 0.157 | — |
| | 5 | 0.471 | — | — | 0.099 | 0.570 | 0.098 |
| | 6 | 0.436 | — | — | 0.128 | 0.564 | 1.207 |
| Eastern kingbird | 1 | 8.068 | 0.190 | T | 0.351 | 8.609 | 0.436 |
| Robin | 1 | 0.677 | 0.062 | 0.030 | 0.047 | 0.816 | 1.002 |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 17.976 | 0.220 | 0.559 | 2.815 | 21.570 | 35.138 |
| | 5 | 96.341 | 1.840 | 0.924 | 26.829 | 125.934 | 56.536 |

NOTE: Blank = sample not analyzed; — indicates none detected; T = trace = <0.001 ppm DDT or <0.002 ppm mirex; all results on fresh-weight basis.

[1] Numbers in parentheses indicate composite of two or more fish or birds.

[2] Samples collected in the Delta.

pesticide may have entered the food chain of human beings. However, additional data involving larger numbers of samples must be collected before any definite statements can be made concerning mirex residues in food products since the possibility of misleading information exists when the number of samples is so small.

When mirex values are compared with DDTR values, it can be seen from Tables 1-4 that in many cases, mirex residue values were found to exceed DDTR values. Among all birds sampled, mirex residues exceeded DDTR residues in 20 of 38 adipose tissues (Table 2b), 10 of 39 liver tissues (Table 2a), and 10 of 37 brain tissues (Table 2c); in fish, mirex values exceeded DDTR values in 4 of 9 adipose samples (Table 2b), in 4 of 7 liver samples (Table 2a), and 1 of 5 muscle samples (Table 2d); similarly, in 6 of 25 arthropod samples (Table 3), mirex values exceeded DDTR values. Additional comparisons between DDTR and mirex values can be made from the information presented in the tables, but the above data are sufficient to illustrate the point that mirex has indeed become a prominent pesticide residue in some wildlife, at least in Mississippi. The existence of some mirex levels which exceed DDTR levels is somewhat surprising since the mirex has been applied at rates which represent grams of toxicant per acre, whereas DDT has been applied at a rate of several pounds per acre, although not necessarily in the area studied. DDT has also been used for a much longer period of time than mirex.

TABLE 2c.—*Mirex and DDT residues in brain tissue of birds collected in Oktibbeha, Noxubee, and Lowndes Counties, Mississippi—1970*

| Specimen | Sample Number | Residues in ppm | | | | | |
|---|---|---|---|---|---|---|---|
| | | *p,p'*-DDE | *p,p'*-DDD | *o,p'*-DDT | *p,p'*-DDT | DDTR | Mirex |
| Chicken | 1 | 0.049 | — | — | — | 0.049 | 0.029 |
| Bobwhite quail | 1 | — | 0.002 | — | — | 0.002 | — |
| | 2 | 0.014 | — | — | — | 0.014 | T |
| | 3 | 0.028 | 0.003 | 0.007 | 0.015 | 0.053 | 0.012 |
| | 4 | 0.009 | — | — | 0.013 | 0.022 | — |
| | 5 | 0.010 | — | — | — | 0.010 | — |
| | 6 | 0.226 | T | T | 0.052 | 0.278 | 0.045 |
| | 7 | 0.010 | — | — | — | 0.010 | — |
| | 8 | 0.015 | — | — | — | 0.015 | — |
| | 9 | 0.008 | — | — | — | 0.008 | — |
| | 10 | 0.008 | — | — | — | 0.008 | — |
| | 11 | | | | | | |
| | 12 | | | | | | |
| | 13 | 0.012 | T | T | T | 0.012 | T |
| | 14 | 0.036 | T | T | T | 0.036 | T |
| | 15 | 0.029 | T | T | T | 0.029 | 0.093 |
| | 16 | 0.008 | — | — | — | 0.008 | T |
| | 17 | 0.008 | T | T | T | 0.008 | T |
| | 18 | 0.017 | T | T | T | 0.017 | — |
| | 19 | 0.019 | — | — | — | 0.019 | — |
| | 20 | 0.019 | — | — | — | 0.019 | 0.067 |
| Brown thrasher | 1 | 0.595 | — | — | 0.043 | 0.638 | 0.318 |
| | 2 | 0.244 | — | — | — | 0.244 | 0.429 |
| | 3 | 1.256 | — | — | 0.086 | 1.342 | 1.057 |
| | 4 | 0.281 | — | — | 0.022 | 0.303 | 0.374 |
| Blue jay | 1 | 0.486 | — | — | — | 0.486 | 1.195 |
| | 2 | 0.118 | — | — | 0.011 | 0.129 | 0.099 |
| | 3 | 0.396 | — | 0.010 | 0.030 | 0.436 | 1.513 |
| Meadow lark | 1 | 0.080 | 0.002 | 0.003 | 0.016 | 0.101 | 0.462 |
| | 2 | 0.338 | T | T | 0.031 | 0.369 | 0.524 |
| Turkey | 1 | 0.009 | — | — | — | 0.009 | — |
| | 2 | | | | | | |
| | 3 | 0.015 | — | 0.002 | 0.008 | 0.025 | — |
| | 4 | | | | | | |
| | 5 | | | | | | |
| | 6 | 0.031 | — | 0.002 | 0.008 | 0.041 | 0.028 |
| Eastern kingbird | 1 | 1.305 | 0.016 | — | 0.071 | 1.392 | 0.029 |
| Robin | 1 | | | | | | |
| | 2 | 1.381 | 0.698 | 0.078 | 2.197 | 4.354 | 0.197 |
| | 3 | 9.819 | 1.238 | 0.138 | 2.521 | 13.716 | 0.172 |
| | 4 | 0.171 | 0.032 | — | 0.031 | 0.234 | 0.404 |
| | 5 | 1.057 | 0.033 | 0.039 | 0.180 | 1.309 | 0.572 |
| Barred owl | 1 | 1.651 | 0.010 | — | 0.032 | 1.703 | 1.820 |

NOTE: Blank = samples not analyzed; — indicates none detected; T = trace = <0.001 ppm DDT or <0.002 ppm mirex; all results on fresh-weight basis.

TABLE 2d.—*Mirex and DDT residues in heart and muscle tissue of fish and birds collected in Oktibbeha, Noxubee, and Lowndes Counties, Mississippi—1970*

| Specimen | Sample Number[1] | Tissue | Residues in ppm | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *p,p'*-DDD | *p,p'*-DDE | *o,p'*-DDT | *p,p'*-DDT | DDTR | Mirex |
| **Fish** | | | | | | | | |
| Channel catfish | 3(2) | Muscle | — | 0.016 | 0.026 | 0.030 | 0.072 | 0.060 |
| | 4(2) | Muscle | — | 0.024 | — | — | 0.024 | 0.079 |
| | 5 | Muscle | 0.118 | 0.105 | 0.083 | 0.142 | 0.448 | — |
| | [2]6 | Muscle | 0.121 | 0.219 | 0.037 | 0.160 | 0.537 | — |
| | [2]7 | Muscle | 0.327 | 0.251 | 0.289 | 0.449 | 1.316 | — |
| **Birds** | | | | | | | | |
| Meadow lark | 1 | Heart | 0.004 | 0.113 | 0.005 | 0.041 | 0.163 | 1.058 |
| | 2 | Heart | T | 0.911 | T | 0.045 | 0.956 | 1.931 |
| Turkey | 5 | Heart | — | 0.018 | 0.002 | 0.010 | 0.030 | 0.020 |
| | 6 | Heart | — | 0.636 | — | 0.117 | 0.753 | 0.127 |
| | 7 | Heart | — | 0.029 | — | T | 0.029 | 0.229 |
| Barred owl | 1 | Muscle | 0.005 | 1.036 | — | 0.020 | 1.061 | 0.934 |

NOTE: —indicates none detected; T=trace=<0.001 ppm DDT or <0.002 ppm mirex; all results on fresh-weight basis.
[1] Numbers in parentheses indicate composite of two or more samples.
[2] Samples collected in the Delta.

TABLE 3.—*Mirex and DDT residues in arthropods collected in Oktibbeha County, Mississippi—1970*

| Specimen | Number of Individuals per Sample | Residues in ppm | | | | | |
|---|---|---|---|---|---|---|---|
| | | *p,p'*-DDD | *p,p'*-DDE | *o,p'*-DDT | *p,p'*-DDT | DDTR | Mirex |
| Praying mantis | 3 | 0.001 | 0.008 | 0.003 | 0.010 | 0.022 | 0.008 |
| Walking sticks | 4 | 0.002 | 0.003 | 0.004 | 0.006 | 0.015 | 0.021 |
| Stink bugs | 19 | 0.004 | 0.061 | 0.018 | 0.048 | 0.131 | — |
| Lady bugs | 15 | 0.012 | 0.692 | 0.039 | 0.052 | 0.793 | — |
| Beetles | 17 | 0.003 | 0.033 | 0.020 | 0.048 | 0.131 | — |
| Spiders | 5 | 0.040 | 0.368 | 0.336 | 0.308 | 1.052 | 1.219 |
| Spider | 1 | — | 0.017 | 0.019 | 0.013 | 0.049 | 0.065 |
| Spider | 1 | — | 0.010 | 0.014 | 0.016 | 0.040 | 0.267 |
| Spider | 1 | — | 0.015 | 0.020 | 0.029 | 0.064 | 0.189 |
| Katydid | 2 | — | 0.011 | 0.019 | 0.029 | 0.059 | — |
| Katydid | 2 | — | 0.007 | 0.019 | 0.017 | 0.043 | — |
| Cricket | 2 | — | 0.013 | 0.016 | 0.052 | 0.081 | 0.008 |
| Cricket | 2 | 0.049 | 0.049 | 0.013 | 0.240 | 0.351 | 0.030 |
| Cricket | 2 | 0.007 | 0.010 | 0.016 | 0.022 | 0.055 | — |
| Cricket | 2 | — | 0.012 | 0.011 | 0.031 | 0.054 | — |
| Cricket | 2 | — | 0.012 | 0.042 | 0.042 | 0.075 | 0.026 |
| Cricket | 2 | — | — | — | — | — | 0.075 |
| Cricket | 2 | — | 0.005 | 0.022 | 0.017 | 0.044 | — |
| Cricket | 2 | — | — | — | — | — | — |
| Cricket | 2 | — | 0.006 | 0.009 | — | 0.015 | — |
| Cricket | 2 | 0.007 | 0.012 | — | — | 0.019 | — |
| Grasshopper | 1 | — | — | 0.034 | 0.033 | 0.067 | — |
| Grasshopper | 2 | — | — | 0.010 | 0.019 | 0.029 | — |
| Grasshopper | 2 | 0.021 | — | 0.030 | 0.019 | 0.049 | — |
| Grasshopper | 4 | 0.077 | 0.011 | 0.012 | 0.015 | 0.038 | — |

NOTE: —indicates none detected; all results on fresh-weight basis.

It is difficult at the present time to assess the implications of the results reported in the present paper. Lacking in most reports to date is any information pertaining to the buildup of mirex in animals following treatment with mirex and what toxic effects, if any, can be expected at various tissue levels. A number of $LD_{50}$ values have been established for mirex and these values indicate that mirex is rather low in its toxicity to animals. Gaines and Kimbrough (*6*), for example, in a study of the toxicity of mirex to rats found the single dose $LD_{50}$ to be 365 mg/kg for adult female rats. The 90-dose $LD_{50}$, the amount daily given in a single dose for 90 days which will result in 50% mortality, was reported to be 6 mg/kg. Earlier, Gaines (*7*) found that when corn oil was used as the carrier, the oral $LD_{50}$ for mirex in male and female rats was 740 and 600 mg/kg, respectively. Mirex administered in a peanut oil solution resulted in a $LD_{50}$ value greater than 3,000 mg/kg, in males and females alike. The pronounced difference in the $LD_{50}$ values found, based on which carrier was used, has not been explained.

TABLE 4.—*Mirex and DDT residues in miscellaneous samples collected in Lowndes and Oktibbeha Counties, Mississippi—1970*

| Specimen | Sample Number[1] | Residues in ppm | | | | | |
|---|---|---|---|---|---|---|---|
| | | *p,p'*-DDD | *p,p'*-DDE | *o,p'*-DDT | *p,p'*-DDT | DDTR | Mirex |
| Cattle egret eggs | 1 | 0.056 | 0.759 | 0.017 | 0.089 | 0.921 | 1.555 |
| | 2 | 0.011 | 0.834 | 0.013 | 0.044 | 0.902 | 0.035 |
| | 3 | 0.012 | 1.944 | — | 0.014 | 2.070 | 0.285 |
| | 4 | 0.024 | 1.769 | 0.014 | 0.353 | 2.160 | 0.055 |
| | 5 | 0.068 | 2.605 | 0.042 | 0.230 | 2.945 | 0.277 |
| | 6 | 0.006 | 0.655 | 0.011 | 0.036 | 0.708 | 0.618 |
| | 7 | 0.018 | 0.302 | 0.022 | 0.139 | 0.481 | 0.073 |
| Blue heron eggs | 1 | 0.084 | 1.561 | 0.031 | 0.605 | 2.281 | 0.051 |
| | 2 | 0.049 | 0.511 | 0.097 | 0.239 | 0.896 | 0.166 |
| | 3 | 0.053 | 3.479 | 0.406 | 0.517 | 4.455 | 0.316 |
| | 4 | 0.012 | 0.220 | 0.017 | 0.062 | 0.311 | T |
| | 5 | 0.010 | 0.369 | 0.017 | 0.059 | 0.455 | 0.083 |
| | 6 | 0.075 | 1.139 | 0.098 | 0.562 | 1.874 | 0.694 |
| Cow's milk (lipid basis) | 1 | 0.003 | 0.013 | T | 0.007 | 0.023 | 0.007 |
| | 2 | — | 0.007 | — | — | 0.007 | 0.016 |
| | 3 | 0.056 | 0.291 | — | 0.054 | 0.401 | — |
| Earthworms | 1 | — | 0.005 | — | — | 0.005 | 0.030 |
| | 2(10) | 0.005 | 0.005 | T | 0.008 | 0.018 | 0.076 |
| Beef adipose | 1 | 0.013 | 0.134 | — | 0.067 | 0.214 | 0.012 |
| | 2 | 0.023 | 0.118 | — | 0.074 | 0.215 | — |
| | 3 | 0.035 | 0.868 | — | 0.068 | 0.971 | 0.113 |
| | 4 | 0.021 | 0.227 | — | 0.055 | 0.303 | 0.042 |
| | 5 | 0.156 | 1.324 | 0.019 | 0.410 | 1.909 | — |
| Silage (dry weight) | 1 | 0.015 | 0.011 | — | — | 0.026 | — |
| | 2 | 0.016 | 0.011 | — | — | 0.027 | — |
| Fescue (dry weight) | 1 | 0.003 | 0.010 | 0.012 | 0.037 | 0.062 | — |

NOTE: —indicates none detected; T=trace=<0.001 ppm DDT or <0.002 ppm mirex; all results on fresh-weight basis unless otherwise noted.
[1] Numbers in parentheses indicate composite of two or more samples.

Ware and Good (*8*) found that a rather low level of mirex in the diet (10 ppm) of mice resulted in 100% mortality by 60 days. This report also showed that 5 ppm of mirex increased parent mortality and decreased litter size.

In addition to mortality data on mammalian species, some evidence has been accumulated which suggests that toxic effects can be produced in mammals following mirex ingestion. Gaines and Kimbrough found that female rats fed 25 ppm of mirex exhibited ultrastructural changes in liver tissue (*6*). Also, some offspring from females fed 25 ppm for 102 days developed cataracts; the incidence of cataracts at this level, which correspond to an average intake of 2.3 mg/kg/day, was 46%.

In relating the findings reported for avian species in the current report to previous work, one must rely on amounts of mirex reported which cause mortality. Toxicity data on a number of different species of birds are given in Circular 199 of the Fish and Wildlife Service (*9*). Data in that publication show that 12% mortality was produced in quail fed 300 ppm for 111 days; young mallards fed a diet containing 500 ppm of mirex experienced a maximum of 81% mortality in 30 days; 20% mortality was observed in pheasants fed a diet which contained 200 ppm of mirex for 30 days; and 8% of a group of cowbirds fed 500 ppm of mirex died after 30 days.

In addition to mortality data, it has been shown that when mirex (600 ppm) was fed to laying hens over a 16-week period, the hens lost weight and the hatchability of eggs and survival of chicks was reduced (*10*). Based on the high amounts of mirex required to reach an $LD_{50}$ or to produce toxic effects, it would not appear that the levels of mirex observed in animals sampled in the current investigation represent a potential hazard.

The most relevant information reported regarding effects of mirex in fish is that provided by Van Valin *et al.* (*11*). These workers showed that lesions in gills and kidneys of goldfish occurred following feeding of mirex. Tissue levels of mirex in goldfish at completion of the experiment ranged from 0 to 1,350 ppm in liver tissue and ranged from 20.8 to 232 ppm in muscle tissue. These fish had been exposed to 1.0 ppm mirex in water for 224 days. The levels reported by Van Valin *et al.* which resulted in histological changes in fish are considerably higher than the values for mirex residues found for the same tissues in the limited number of fish samples in the current investigations.

To summarize the above discussion, it appears that for the most part mirex is low in its toxicity to animals based

on $LD_{50}$ values. However, rather low amounts of this material in the diet of some animals, mice for example, can produce mortality. Because of the lack of information regarding tissue levels of mirex encountered with the feeding of $LD_{50}$ dosages, it is not possible to interpret the meaning of the levels observed in samples discussed in this report, although some previous data on fish indicate that the values reported in the current study do not represent toxic levels.

*Acknowledgment*

The authors are indebted to Mr. Burton S. Webster and the staff of the Noxubee Wildlife Refuge for the assistance given in obtaining samples. Special thanks is extended to the many technicians who assisted in the pesticide analyses.

See Appendix for chemical names of compounds discussed in this paper.

This work was supported in part by funds provided by the Public Health Service, Food and Drug Administration, Department of Health, Education, and Welfare, under contract FDA 71-6.

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# Chemical Residues in Lake Erie Fish—1970-71 [1]

Richard L. Carr, Charles E. Finsterwalder, and Michael J. Schibi


## ABSTRACT

*Yellow perch, coho salmon, carp, channel catfish, freshwater drum, and white bass from the Ohio shore of Lake Erie were analyzed during 1970-71 for residues of chlorinated pesticides (DDE, TDE, DDT, and dieldrin), polychlorinated biphenyls (PCB's), and mercury. All but 1 of the 80 samples analyzed contained DDT and/or its metabolites; PCB's were found in all samples. Fifty-three of the 80 samples were analyzed for mercury, and all were found positive.*

*Average levels of residues for the species sampled ranged from 0.06 to 0.42 ppm for DDE; 0.07 to 0.52 ppm, TDE; 0.03 to 0.25 ppm, DDT; 0.18 to 0.90 ppm, total DDT; 0.01 to 0.07 ppm, dieldrin; 0.08 to 4.4 ppm, PCB's; and 0.12 to 0.64 ppm, mercury. The highest average residue levels of total DDT were in coho salmon and channel catfish. Average levels of PCB's were significantly higher in channel catfish, and levels of mercury were significantly higher in white bass.*


## *Introduction*

In the spring of 1970 the Cincinnati District of the U. S. Food and Drug Administration began monitoring yellow perch (*Perca flavescens*) and, in cooperation with the Ohio Department of Natural Resources, Division of Wildlife, coho salmon (*Oncorhynchus kisutch*) to determine the extent of pesticide contamination in these species in Lake Erie. The next spring (1971) monitoring was broadened to include white bass (*Roccus chrysops*), freshwater drum (*Aplodinotus grunniens*), channel catfish (*Ictalurus punctatus*), and carp (*Cyprininus carpio*). These six species were selected because they had the greatest commercial significance and/or greatest potential for residues due to their predatory eating habits and size. The investigation of these species was limited to the Ohio shore of Lake Erie, since this was the legal boundary of Cincinnati District of FDA.

Prior to the expansion of the program (1970), the coho salmon and yellow perch (15 and 12 samples, respectively) were analyzed for DDT and its isomers and metabolites, dieldrin, and PCB's (calculated as Aroclor® 1254); after the expansion (1971), all species were analyzed for mercury as well.

## *Sampling Procedures*

The coho salmon, collected by the Ohio Division of Wildlife, were random samples and represented catches from almost the entire Ohio shore of Lake Erie (Fig. 1); the other species were collected by Food and Drug inspectors at commercial fisheries in Ohio. The coho salmon represent catches on a year-round basis, while the other species were obtained during the fishing season on Lake Erie, a period from latter March to early October. Each coho sample consisted of 1 or 2 fish and the other samples consisted of 5 to 10 fish.

On collection, the samples were frozen and shipped to the laboratory in Cincinnati. At the laboratory, the samples were thawed, and the heads, viscera, and scales removed. The rest of the fish was then thoroughly ground and mixed in a meat grinder.

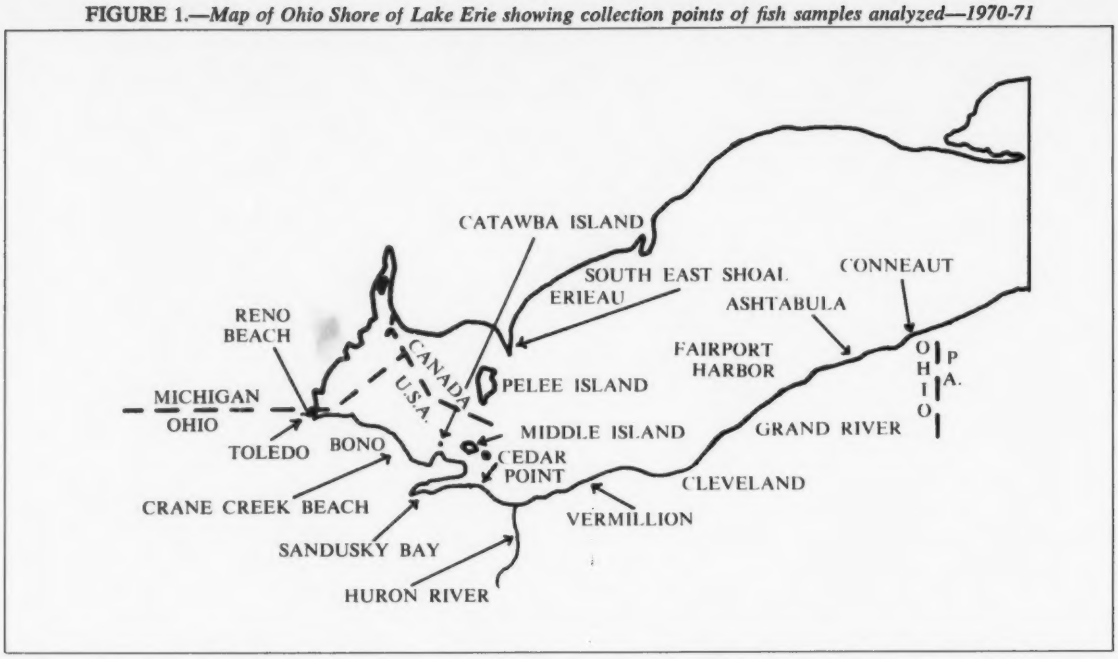
## *Analytical Procedures*

### ORGANOCHLORINES AND PCB'S

The method employed for extraction and cleanup of samples to determine DDT residues, dieldrin, and PCB's was that described by Porter, Young, and Burke (*6*). The procedure involved dehydrating the sample with sodium sulfate and then isolating the fat by blending 50 g of the sample three times with petroleum ether. The fat was partitioned with acetonitrile and the residues isolated by a Florisil column, eluted with 6% and 15% ethyl petroleum ether. The 15% eluate which contained any residues of dieldrin was additionally cleaned up using alkaline saponification (*4*). PCB residues in the

[1] From the U. S. Food and Drug Administration, 1141 Central Parkway, Cincinnati, Ohio 45202.

FIGURE 1.—*Map of Ohio Shore of Lake Erie showing collection points of fish samples analyzed—1970-71*




6% eluate were isolated from DDT residues by using the silicic acid column method described by Armour and Burke (*1*).

A Barber-Coleman Model 10 gas-liquid chromatograph (GLC), equipped with a 150-mc tritium electron capture detector, was used for all quantitative assays (*4*). Two columns were used: (1) 10% DC-200 on Chromosorb W/HP and (2) a 1 to 1 mixture of 10% DC-200 and 15% QF-1 on Chromosorb W/HP. Parameters were those given in the FDA Pesticide Analytical Manual (*3*).

Confirmation tests for the chlorinated pesticide residues consisted of thin layer chromatography (*3*) of 10 randomly selected samples. PCB residues were confirmed by their stability to alkaline saponification and by microcoulometric GLC using a chlorine specific detector (*3*). Quantitation of pesticide residues was accomplished using peak height. PCB residues in the fish had a pattern most similar to Aroclor® 1254 and were calculated by comparing the entire area of the PCB pattern with the area of Aroclor® 1254. Standards were supplied by the FDA Pesticide Reference Standard Section.

Recovery data for the above procedure provided by Carr in a collaborative study (*2*) were *p,p'*-DDE, 87.5 ± 13.5%; *p,p'*-TDE, 88.6 ± 11.4%; *p,p'*-DDT, 90.6 ± 9.7%; and dieldrin 82.2 ± 25.4%.

### MERCURY

Mercury was determined using the method described and collaborated by Munns and Holland (*5*). The method employs a perchloric acid digestion and subsequent determination by "cold vapor" atomic absorption. The instrument was a Perkin-Elmer Model 303 AA with a 17-cm cell length in a closed system. The 2533 A absorption line was used. The average recovery for samples fortified with methyl mercury chloride was 85.4%.

## *Results*

Table 1 lists the individual residue levels for each fish sample in the study by species; Table 2 summarizes these results. These data were not corrected for percent recovery, and the minimum level recorded in all determinations was 0.01 ppm; all residues are reported on a wet-weight basis. Average residues of total DDT were highest in coho salmon (0.90 ppm) and catfish (0.89 ppm); however, none of the samples approached the FDA guideline of 5 ppm. Average dieldrin residues were highest in coho salmon (0.07 ppm), although again the levels were low. Polychlorinated biphenyl residues were significantly higher in channel catfish (average 4.4 ppm). White bass continued the highest average level of mercury with residues in five of the six white bass samples examined in excess of FDA's 0.5 ppm guideline. In general, the species lowest in the food chain, yellow perch, and the "rougher" fish (fish that are not sport fish or of significant food value), carp and freshwater drum contained the lowest amounts of chemical residues.

See Appendix for chemical names of compounds discussed in this paper.

TABLE 1.—*Chemical residue levels in six species of fish, Lake Erie—1970-71*

| Location of Catch | Date Collected[1] | Residues in ppm | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | DDE | TDE | DDT | Total DDT | Dieldrin | PCB's | Mercury |
| **COHO SALMON** | | | | | | | | |
| Sandusky Bay (I) | 4/1/70 | 0.39 | 0.15 | 0.25 | 0.79 | 0.06 | 1.6 | |
| Sandusky Bay (M) | 4/1/70 | 0.38 | 0.28 | — | 0.66 | 0.06 | 1.7 | |
| Sandusky Bay (I) | 4/1/70 | 0.34 | 0.10 | 0.31 | 0.75 | 0.05 | 1.6 | |
| NNW Toledo (M) | 5/18/70 | 0.32 | 0.28 | 0.18 | 0.78 | 0.07 | 1.3 | |
| NNW Toledo (M) | 5/18/70 | 0.32 | 0.15 | 0.37 | 0.84 | 0.06 | 1.0 | |
| NNW Toledo (M) | 5/18/70 | 0.43 | — | 0.67 | 1.10 | 0.08 | 2.2 | |
| East Pelee Island (M)[2] | 6/10/70 | 0.62 | 0.45 | 0.23 | 1.30 | 0.08 | 2.6 | |
| East Pelee Island (M) | 6/10/70 | 0.53 | 0.32 | 0.23 | 1.09 | 0.06 | 1.6 | |
| Southeast Shoal | 6/30/70 | 0.72 | 0.21 | 0.38 | 1.31 | 0.06 | 3.2 | |
| Southeast Shoal | 6/30/70 | 0.64 | 0.25 | 0.50 | 1.39 | 0.06 | 3.2 | |
| Southeast Shoal (I) | 6/30/70 | 0.55 | 0.42 | 0.11 | 1.08 | 0.05 | 4.3 | |
| NE Erieau Ontario (M) | 7/28/70 | 0.39 | 0.25 | 0.04 | 0.68 | 0.05 | 1.5 | |
| NE Erieau Ontario (M) | 7/28/70 | 0.88 | 0.50 | 0.07 | 1.45 | 0.15 | 3.1 | |
| NE Erieau Ontario (M) | 7/28/70 | 0.60 | 0.42 | 0.15 | 1.17 | 0.10 | 3.8 | |
| W Erieau Ontario (M) | 7/30/70 | 0.90 | 0.30 | 0.49 | 1.69 | 0.14 | 3.2 | |
| NE Fairport Harbor (M) | 8/1/70 | 0.53 | 0.23 | 0.50 | 1.26 | 0.07 | 2.2 | 0.42 |
| NE Fairport Harbor (M) | 8/11/70 | 0.27 | 0.20 | 0.24 | 0.71 | 0.06 | 1.6 | 0.59 |
| NE Fairport Harbor (M) | 8/11/70 | 0.31 | 0.18 | 0.06 | 0.55 | 0.03 | 1.3 | 0.39 |
| N Conneaut (M) | 9/2/70 | 0.04 | 0.46 | 0.13 | 0.63 | 0.09 | 3.8 | 0.58 |
| N Conneaut (M) | 9/2/70 | 0.06 | 0.25 | 0.61 | 0.91 | 0.06 | 1.5 | 0.21 |
| N Ashtabula (I) | 9/2/70 | 0.17 | 0.17 | 0.44 | 0.78 | 0.05 | 1.10 | 0.11 |
| N Conneaut (I) | 9/3/70 | — | 0.10 | 0.11 | 0.21 | 0.04 | 1.2 | 0.14 |
| W Huron (M) | 10/12/70 | 0.46 | 0.20 | 0.08 | 0.74 | 0.03 | 1.3 | 0.47 |
| W Huron (M) | 10/12/70 | 0.42 | 0.24 | 0.11 | 0.78 | 0.04 | 1.9 | 0.36 |
| W Huron (M) | 10/12/70 | 0.47 | 0.16 | 0.26 | 0.89 | 0.03 | 1.2 | 0.20 |
| Huron River Dam (M) | 11/4/70 | 0.47 | 0.22 | 0.10 | 0.79 | 0.04 | 2.9 | 0.35 |
| Huron River Dam (M) | 12/8/70 | 0.37 | 0.21 | 0.07 | 0.65 | 0.03 | 2.6 | 0.41 |
| Sandusky Bay (I) | 4/1/71 | 0.28 | 0.16 | 0.11 | 0.53 | 0.07 | 1.1 | 0.24 |
| Bono (M) | 4/23/71 | 0.50 | — | 0.50 | 1.00 | 0.10 | 1.4 | 0.12 |
| Middle Island (M) | 6/14/71 | 0.21 | 0.22 | 0.07 | 0.50 | 0.07 | 2.6 | 0.36 |
| **YELLOW PERCH** | | | | | | | | |
| North of Cleveland | 4/13/70 | 0.04 | 0.03 | — | 0.09 | 0.02 | 0.5 | |
| North of Fairport | 4/19/70 | — | — | — | — | — | 0.26 | |
| Sandusky Bay | 4/30/70 | 0.05 | 0.05 | 0.05 | 0.15 | 0.02 | 0.6 | |
| Catawba Island | 5/13/70 | 0.08 | 0.06 | — | 0.14 | — | 1.1 | |
| ENE of Toledo | 5/16/70 | 0.08 | 0.06 | 0.07 | 0.21 | — | 0.8 | |
| Crane Creek-Toledo | 5/17/70 | 0.09 | 0.07 | — | 0.16 | — | 1.2 | |
| NW Conneaut | 5/18/70 | 0.17 | 0.05 | 0.13 | 0.35 | — | 0.8 | |
| NE Cleveland | 5/18/70 | 0.08 | 0.05 | 0.11 | 0.24 | — | 0.8 | |
| East of Conneaut | 6/15/70 | 0.09 | 0.03 | 0.05 | 0.17 | — | 0.5 | |
| North of Cleveland | 6/16/70 | 0.10 | 0.08 | 0.06 | 0.24 | — | 0.8 | |
| East of Reno Beach | 6/16/70 | 0.10 | 0.11 | — | 0.21 | — | 1.3 | |
| East of Reno Beach | 7/14/70 | 0.14 | 0.15 | 0.05 | 0.34 | 0.02 | 0.9 | |
| East of Cedar Point | 8/18/70 | 0.02 | 0.04 | — | 0.09 | — | 0.2 | 0.15 |
| North of Conneaut | 8/26/70 | 0.06 | 0.08 | 0.20 | 0.34 | — | 0.5 | 0.22 |
| East of Toledo | 9/15/70 | — | 0.19 | 0.11 | 0.30 | — | 2.4 | 0.37 |
| NW of Vermillion | 10/5/70 | 0.06 | 0.05 | 0.04 | 0.15 | 0.02 | 0.6 | 0.25 |
| Ashtabula | 10/7/70 | 0.04 | 0.05 | 0.07 | 0.16 | 0.02 | 0.2 | 0.16 |
| East of Toledo | 10/8/70 | 0.08 | 0.10 | 0.02 | 0.20 | 0.01 | 0.9 | 0.40 |
| Grand River | 11/18/70 | 0.03 | 0.04 | — | 0.07 | — | 0.7 | 0.13 |
| Sandusky Bay | 3/29/71 | 0.05 | 0.07 | 0.02 | 0.14 | 0.01 | 0.8 | 0.25 |
| ENE of Toledo | 3/30/71 | 0.06 | 0.10 | 0.01 | 0.17 | 0.01 | 0.8 | 0.45 |
| Conneaut | 5/11/71 | 0.02 | 0.04 | 0.03 | 0.09 | 0.01 | 0.4 | 0.16 |
| Vermillion | 5/13/71 | 0.05 | 0.03 | 0.03 | 0.11 | 0.01 | 0.5 | 0.19 |
| **WHITE BASS** | | | | | | | | |
| Cedar Point | 8/11/70 | 0.24 | 0.27 | 0.13 | 0.64 | 0.06 | 2.1 | 0.62 |
| East of Toledo | 9/15/70 | 0.02 | 0.30 | 0.05 | 0.37 | 0.03 | 3.5 | 0.70 |
| Sandusky Bay | 9/23/70 | 0.26 | 0.30 | 0.31 | 0.87 | 0.03 | 1.9 | 0.60 |
| East of Toledo | 10/12/70 | 0.11 | 0.22 | 0.10 | 0.43 | 0.03 | 1.4 | 0.58 |
| Vermillion | 3/29/71 | 0.33 | 0.34 | 0.06 | 0.73 | 0.06 | 2.4 | 0.86 |
| ENE of Toledo | 3/30/71 | 0.11 | 0.21 | 0.02 | 0.34 | 0.03 | 1.6 | 0.45 |

TABLE 1.—*Chemical residue levels in six species of fish, Lake Erie—1970-71*—Continued

| Location of Catch | Date Collected[1] | Residues in ppm | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | DDE | TDE | DDT | Total DDT | Dieldrin | PCB's | Mercury |
| **CARP** | | | | | | | | |
| East of Cedar Point | 8/18/70 | 0.04 | 0.08 | — | 0.12 | — | 0.4 | 0.07 |
| East of Toledo | 9/15/70 | 0.02 | 0.06 | 0.02 | 0.10 | — | 0.3 | 0.11 |
| Sandusky Bay | 9/23/70 | — | 0.39 | 0.12 | 0.51 | 0.02 | 0.9 | 0.16 |
| East of Toledo | 10/8/70 | 0.14 | 0.24 | 0.04 | 0.38 | 0.05 | 4.3 | 0.08 |
| Vermillion | 3/13/71 | 0.61 | 0.26 | 0.04 | 0.91 | 0.06 | 5.3 | 0.13 |
| Vermillion | 3/20/71 | 0.11 | 0.21 | — | 0.32 | 0.04 | 1.1 | 0.17 |
| ENE of Toledo | 3/30/71 | 0.13 | 0.32 | — | 0.45 | 0.04 | 2.3 | 0.12 |
| **CHANNEL CATFISH** | | | | | | | | |
| East of Cedar Point | 8/18/70 | 0.53 | 0.66 | 0.12 | 1.41 | 0.10 | 3.9 | 0.31 |
| East of Toledo | 9/15/70 | 0.07 | 0.85 | 0.26 | 1.18 | 0.05 | 4.7 | 0.45 |
| Sandusky Bay | 9/23/70 | 0.04 | 0.09 | 0.09 | 0.22 | 0.01 | 1.4 | 0.14 |
| East of Toledo | 10/8/70 | 0.43 | 0.65 | 0.13 | 1.21 | 0.07 | 4.2 | 0.72 |
| ENE of Toledo | 3/30/71 | 0.28 | 0.46 | 0.06 | 0.80 | 0.07 | 6.2 | 0.48 |
| Sandusky Bay | 4/23/71 | 0.38 | 0.33 | 0.06 | 0.77 | 0.04 | 2.4 | 0.32 |
| Vermillion | 5/12/71 | — | 0.59 | 0.15 | 0.74 | 0.04 | 7.8 | 0.49 |
| **FRESHWATER DRUM** | | | | | | | | |
| Cedar Point | 8/18/70 | 0.08 | 0.11 | — | 0.19 | — | 0.8 | 0.40 |
| East of Toledo | 9/15/70 | 0.12 | 0.19 | 0.09 | 0.40 | — | 1.4 | 0.45 |
| Sandusky Bay | 9/23/70 | — | 0.08 | 0.02 | 0.10 | 0.02 | 0.6 | 0.21 |
| East of Toledo | 10/8/70 | 0.17 | 0.18 | 0.12 | 0.47 | 0.02 | 1.3 | 0.37 |
| Vermillion | 3/29/71 | 0.08 | 0.10 | 0.04 | 0.22 | 0.04 | 0.8 | 0.24 |
| ENE of Toledo | 3/30/71 | 0.09 | 0.15 | 0.02 | 0.26 | 0.03 | 1.2 | 0.43 |
| Vermillion | 5/12/71 | 0.17 | 0.11 | 0.15 | 0.43 | 0.05 | 1.5 | 0.29 |

NOTE: — = not detected; blank = not analyzed.
(M) = Mature fish; (I) = Immature fish.

[1] Although the monitoring program was not expanded to include carp, channel catfish, freshwater drum, and white bass until 1971, some of the analyses were done on samples collected in 1970.

[2] Although sample was found to be a chinook salmon, it was not eliminated from the study.

TABLE 2.—*Average and range of chemical residue levels in six species of fish, Lake Erie—1970-71*

| Species | Number of Samples | Residues in PPM | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | DDE | | TDE | | DDT | | Total DDT | | Dieldrin | | PCB's | | Mercury | |
| | | Avg. | Range | Avg. | Range | Avg. | Range | Avg. | Range | Avg. | Range | Avg. | Range | Avg. | Range |
| Coho salmon | 30/15[1] | 0.42 | 0.04-0.90 | 0.24 | 0.00-0.50 | 0.25 | 0.00-0.67 | 0.90 | 0.21-1.69 | 0.07 | 0.03-0.15 | 2.1 | 1.0-4.3 | 0.32 | 0.11-0.59 |
| Yellow perch | 23/11[1] | 0.06 | 0.00-0.17 | 0.07 | 0.00-0.19 | 0.05 | 0.00-0.20 | 0.18 | 0.07-0.35 | 0.01 | 0.00-0.02 | 0.8 | 0.2-2.4 | 0.25 | 0.13-0.45 |
| White bass | 6 | 0.18 | 0.02-0.33 | 0.27 | 0.21-0.34 | 0.11 | 0.02-0.31 | 0.56 | 0.34-0.87 | 0.04 | 0.03-0.06 | 2.1 | 1.4-3.5 | 0.64 | 0.45-0.86 |
| Carp | 7 | 0.15 | 0.00-0.61 | 0.22 | 0.06-0.39 | 0.03 | 0.00-0.12 | 0.40 | 0.10-0.91 | 0.04 | 0.00-0.06 | 2.0 | 0.3-5.3 | 0.12 | 0.07-0.17 |
| Channel catfish | 7 | 0.25 | 0.00-0.53 | 0.52 | 0.09-0.85 | 0.12 | 0.06-0.26 | 0.89 | 0.22-1.31 | 0.05 | 0.01-0.10 | 4.4 | 1.4-7.8 | 0.42 | 0.14-0.72 |
| Freshwater drum | 7 | 0.10 | 0.00-0.17 | 0.13 | 0.08-0.19 | 0.06 | 0.00-0.15 | 0.30 | 0.10-0.47 | 0.02 | 0.00-0.05 | 1.1 | 0.6-1.5 | 0.34 | 0.21-0.45 |

[1] Total samples/samples analyzed for mercury.

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# *Mercury and Lead Residues in Starlings—1970* [1]

William E. Martin


## ABSTRACT

*Starling* (Sturnus vulgaris) *samples from 125 randomly selected sites were analyzed for mercury residues. Except for three locations, all samples had residues well below 0.5 ppm. Lead residues were identified in all samples from 23 survey sites that had been tentatively selected to evaluate use of starlings as a biological measure of environmental contamination by lead. Residues of lead ranged from 0.4 to 13.3 ppm with a mean of 3.18 ppm and a standard error of 0.62 ppm.*


## *Introduction*

The starling (*Sturnus vulgaris*) has been used since 1967 by the Bureau of Sport Fisheries and Wildlife as an indicator species for measuring occurrence and relative amounts of selected persistent environmental contaminants. The overall wildlife monitoring scheme, the randomized nationwide sampling design, and analytical methods used for determining residue levels of persistent organochlorine insecticides, mercury, and lead in starling tissue are described by Dustman *et al.* (*1*) and Martin (*2*).

Determination of mercury residues in starlings is conducted to aid in evaluation of the relative distribution of this element in terrestrial fauna other than game birds. Concern over possible widespread environmental contamination by lead provided the impetus for the preliminary survey of lead residues in starlings. The starling was selected because it is present throughout the contiguous States in both urban and rural areas, it is omnivorous in its feeding habits, and normally is not exposed to lead shotgun pellets.

This report presents lead and mercury residue data gathered from starling monitoring collections made during November and December 1970.

[1] From the Pesticide Appraisal and Monitoring Branch, Division of Wildlife Services, Bureau of Sport Fisheries and Wildlife, U. S. Department of the Interior, Washington, D. C. 20240.

## *Sampling Procedures*

### MERCURY

A randomized, nationwide sampling design was used to obtain birds for mercury analysis. This standard design allows for sampling at up to four randomly selected sites within each of 40 five-degree blocks drawn from 24° to 49° latitude and 64° to 124° longitude, as shown in Fig. 1. Sampling locations are identified by a row number, a column letter, and a site number; e.g., the site near Tacoma, Wash., is designated 1-A-1. Tissues used for mercury analysis in the study reported here were taken from the same bird samples used for persistent organochlorine insecticide analyses reported separately by Martin and Nickerson (*3*). Collections were successful at 125 of the planned 139 sites (Table 1).

### LEAD

A total of 25 sampling sites were selected to reflect the degree of lead residues expected from man's activities and related pollution sources, such as a high incidence of industrialization, heavy automobile traffic, etc. Samples were not obtained from two critical preselected locations—Los Angeles, Calif., a site which was expected to reflect relatively high lead residue, and Carlsbad, N. Mex., predicted to reflect relatively low lead residues. Selected sampling sites are listed in Table 2 with results of lead analyses.

As described by Martin and Nickerson (*3*), each sample normally consisted of a "pool" of 10 birds. "Pools" containing fewer than 10 birds are indicated by footnote in the appropriate tables. Birds analyzed for mercury residues had been either trapped or shot. Starlings collected for lead analysis were taken by means other than lead shot or poison. The bird "pools" were wrapped in aluminum foil, placed in polyethylene bags, and frozen immediately for later laboratory analyses.

FIGURE 1.—*Starling monitoring sites—1970*

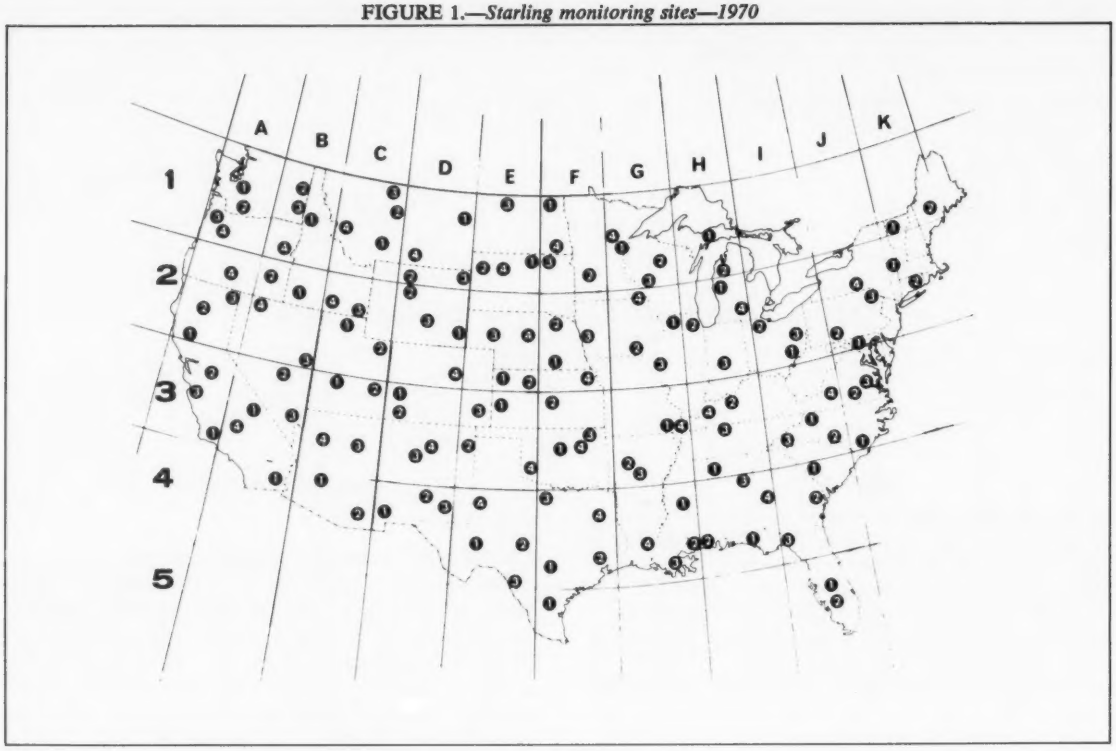


TABLE 1.—*Mercury and lead sampling site locations, 1970*

| State | City or County | Sampling Site Number [1,2] | State | City or County | Sampling Site Number [1,2] |
|---|---|---|---|---|---|
| Alabama | Marion | 3-H-1 | Georgia | Pike | 4-H-4 |
| | Talladega | 4-H-3 | | Wayne | 4-I-2 |
| Arizona | Navajo | 3-C-3 | | Atlanta (Lead) | 19 |
| | Yavapi | 3-C-4 | Idaho | Nezperce | 1-B-1 |
| | Maricopa | 4-C-1 | | Owyhee | 2-B-1 |
| | Graham | 4-C-2 | | Franklin | 2-C-3 |
| | Phoenix (Lead) | 7 | | Minidoka | 2-C-4 |
| Arkansas | Yell/Pope | 3-G-2 | | Boise (Lead) | 5 |
| | Lonoke/Pulaski | 3-G-3 | Illinois | Stephencon | 2-G-1 |
| | Stuttgart (Lead) | 16 | | Sangamon | 2-G-3 |
| California | Colusa | 2-A-1 | | Cook | 2-H-2 |
| | Shasta | 2-A-2 | | Chicago (Lead) | 13 |
| | Modoc | 2-A-3 | Indiana | Henry | 2-H-3 |
| | Ventura | 3-A-1 | Iowa | Pottawattamie | 2-F-3 |
| | Stanislaus | 3-A-2 | | Polk | 2-G-2 |
| | Monterey | 3-A-3 | | Butler | 2-G-4 |
| | Inyo | 3-B-1 | Kansas | Rawlins | 2-E-1 |
| | Kern | 3-B-4 | | Smith | 2-E-2 |
| | Imperial | 4-B-1 | | Hamilton & Kearny | 3-E-1 |
| | Los Angeles (Lead) | 3 | | Nemaha | 2-F-4 |
| Colorado | Adams | 2-D-4 | | Marion | 3-F-2 |
| | Montrose | 3-D-1 | Kentucky | Ohio | 3-H-2 |
| | La Plata & Rio Grande | 3-D-2 | | Hopkins | 3-H-4 |
| | Otero | 3-E-3 | Louisiana | Jefferson | 4-G-3 |
| | Greeley (Lead) | 8 | | Rapides | 4-G-4 |
| Connecticut | New London | 2-K-2 | | Baton Rouge (Lead) | 17 |
| Florida | Bay | 4-H-1 | Maine | Penobscot | 1-K-2 |
| | Madison | 4-I-3 | | Gray (Lead) | 25 |
| | Polk | 5-I-1 | Maryland | Prince Georges | 2-J-1 |
| | Hardee | 5-I-2 | | Patuxent (Lead) | 22 |
| | Gainesville (Lead) | 20 | | | |

TABLE 1.—*Mercury and lead sampling site locations, 1970*—Continued

| State | City or County | Sampling Site Number [1,2] |
|---|---|---|
| Michigan | Chippewa | 1-H-1 |
| | Grand Traverse | 1-H-2 |
| | Kent | 2-H-1 |
| | Inaham | 2-H-4 |
| Minnesota | Swift | 1-F-2 |
| | Pine | 1-G-1 |
| | Aitkin | 1-G-4 |
| | Twin Cities (Lead) | 12 |
| Mississippi | Leake | 4-G-1 |
| | Harrison | 4-G-2 |
| | Jackson | 4-H-2 |
| Missouri | Stoddard | 3-G-1 |
| | Bollinger | 3-G-4 |
| Montana | Meagher | 1-C-1 |
| | Missoula | 1-C-4 |
| | Richland | 1-D-1 |
| | Yellowstone | 1-D-4 |
| Nebraska | Keith | 2-E-3 |
| | Lincoln | 2-E-4 |
| | Clay | 2-F-1 |
| | Antelope | 2-F-2 |
| Nevada | White Pine | 2-B-3 |
| | Humboldt | 2-B-4 |
| | Nye | 3-B-2 |
| | Clark | 3-B-3 |
| | Reno (Lead) | 4 |
| New Mexico | Bernalillo | 3-D-3 |
| | Santa Fe & Torrance | 3-D-4 |
| | Luna | 4-D-1 |
| | Chaves | 4-D-3 |
| | Quay | 3-E-2 |
| | Carlsbad (Lead) | 9 |
| New Jersey | N. Brunswick (Lead) | 23 |
| New York | Oswego | 2-J-4 |
| | Rennselaer | 2-K-1 |
| | Jamestown (Lead) | 24 |
| North Carolina | Wilkes | 3-I-1 |
| | Union | 3-I-2 |
| | Macon | 3-I-3 |
| | Pender | 3-J-1 |
| | Raleigh (Lead) | 21 |
| North Dakota | Ward | 1-E-3 |
| | Cavelier | 1-F-1 |
| | Dickey | 1-F-4 |
| Ohio | Washington | 2-I-1 |
| | Erie | 2-I-2 |
| | Jefferson | 2-I-3 |
| Ohio (Cont'd.) | Sandusky (Lead) | 14 |
| | Columbus (Lead) | 15 |
| Oklahoma | Greer | 3-E-4 |
| | Canadian | 3-F-1 |
| | Nowata | 3-F-3 |
| | Okmulgee | 3-F-4 |
| | Tishomingo (Lead) | 10 |
| Oregon | Yamhill | 1-A-3 |
| | Lane | 1-A-4 |
| | Klamath | 2-A-4 |
| | Baker | 1-B-4 |
| | Harney | 2-B-2 |
| | Corvallis (Lead) | 2 |
| Pennsylvania | Somerset | 2-J-2 |
| | Cuzerne | 2-J-3 |
| South Carolina | Aiken | 4-I-1 |
| South Dakota | Potter | 1-E-1 |
| | Hughes | 1-E-4 |
| | Brown | 1-F-3 |
| | Mitchell (Lead) | 11 |
| Tennessee | Davidson | 3-H-3 |
| | Nashville (Lead) | 18 |
| Texas | Clay | 4-F-3 |
| | Morris | 4-F-4 |
| Utah | Weber | 2-C-1 |
| | Sevier/Millard | 3-C-1 |
| | Salt Lake City (Lead) | 6 |
| Vermont | Addison | 1-K-1 |
| Virginia | Amherst | 3-I-4 |
| | Prince George | 3-J-2 |
| | Caroline | 3-J-3 |
| Washington | Pierce | 1-A-1 |
| | Yakima | 1-A-2 |
| | Spokane | 1-B-2 |
| | Whitman | 1-B-3 |
| | Yakima (Lead) | 1 |
| Wisconsin | Curtiss | 1-G-2 |
| | Trempeleau | 1-G-3 |
| Wyoming | Big Horn | 1-D-2 |
| | Brook | 1-D-3 |
| | Goshen | 2-D-1 |
| | Washakie | 2-D-2 |

[1] Mercury sampling sites are described by the counties in which collections were taken and are identified by a three place site number (e.g., 1-A-1).

[2] Lead samples were taken near the cities indicated in the Table. A single number identified the site locations.

### *Analytical Procedures*

Residue analyses were done by the Wisconsin Alumni Research Foundation [2] under contract with the Bureau of Sport Fisheries and Wildlife. Birds were prepared by skinning and removing the beak and wings at the first joint out from the body; the removed parts were discarded. Each 10-bird "pool" was ground together in a Hobart food chopper, and a subsample taken for analysis by atomic absorption spectrophotometry. Results are reported on a whole body, wet-weight basis.

#### MERCURY

A cold vapor atomic absorption technique was suggested by the contracting laboratory as being more rapid with greater selectivity and less interference. Digestion for this technique was a modification of one reported by the Joint Mercury Residue Panel (*4*). The methodology was demonstrated by the contractor to provide results comparable to the WARF "boat" method for both bird and

[2] Mention of this commercial laboratory is for identification only and does not constitute endorsement by the U. S. Department of the Interior.

fish tissue and was accepted for use. A 25 ml sulfuric-nitric acid mixture (4:1) was added to a 10-g aliquot of the sample, and the mixture was heated slowly for 30 to 45 minutes to reach full temperature; the sample was then refluxed for 1 hour. After the digest had cooled to room temperature, it was transferred to a 100-ml volumetric flask quantitatively with ice water; the container was stoppered, and the sample again was allowed to return to room temperature. Determination was made with a Perkin-Elmer atomic absorption spectrophotometer Model 303 fitted with a cold vapor device and a Perkin-Elmer Model 304 recorder.

Instrument conditions were:

| | |
|---|---|
| Wavelength | 2537 A (Setting 254) |
| Slit | 3 mm, 20 A |
| Range | UV |
| Source | Mercury hollow cathode lamp |
| Air | 3 liters per minute |

Recorder noise suppression—1, expansion—3x

The standard curve used for determination had almost a 20-fold range starting with 0.010 $\mu$g of mercury. The curve was plotted using peak height versus micrograms of mercury.

An 0.5 gram equivalent aliquot was used to measure for mercury for an indicated sensitivity of 0.05 ppm. This was used since this is the level at which natural occurring and background residues could be expected. In terms of practical instrument sensitivity, 0.01 $\mu$g was the lower level of sensitivity for the analytical method. The procedures include methylmercury as part of the total mercury reported.

Recovery studies were conducted on the analytical method using samples not reported in this paper. Recoveries ranged from 86% to 106%. Figures reported in this paper were not corrected for recovery.

LEAD

A 25-g portion of the sample homogenate was dried and charred on a hot plate, then transferred to a 500° C muffle furnace and ashed overnight. The ash was cooled, wet with nitric acid, then taken to dryness, and returned to the muffle for 20 minutes. After the sample was again cooled, 2 ml of concentrated hydrochloric acid and about 15 ml of water were added. The mixture then was brought to a boil, cooled, and made to volume for analysis. Determination was made with a Model 303 Perkin-Elmer atomic absorption spectrophotometer in accordance with standard Perkin-Elmer procedures for lead (*5*).

Instrument settings were:

| | |
|---|---|
| Wavelength | 283.3 background at 280.0 negative |

Recorder noise suppression—3, expansion—3x

Recovery studies were not done for lead analysis. The lower level of sensitivity for lead was 0.1 ppm.

## *Results and Discussion*

MERCURY

Residue levels of mercury in the 125 bird pools analyzed are shown in Table 2. Values are reported for individual sites grouped by 5-degree blocks, and block means are given. These preliminary findings for mercury residues in starlings appear somewhat encouraging in light of recent concern about relatively high residues in a variety of fish and game birds. With the exceptions of two high levels of 1.5 ppm and 1.9 ppm found in northwestern Oregon (1-A-3 and 1-A-4, respectively) and one sample approaching 0.5 ppm in California (2-A-1), the residue levels for mercury in starlings appear to be uniformly low throughout the contiguous United States. Of the 125 samples analyzed, 102 showed levels equal to or less than 0.09 ppm on a whole body, wet-weight basis; 53 of these 102 samples were below the upper value of the World Health Organization's "practical residue limit" (range, 0.02-0.05 ppm) (*8*). The practical residue limit describes residues expected to be found in food from background and natural environmental contamination. Of the 23 samples in which mercury was found in excess of 0.09 ppm, only the 3 West Coast samples (1-A-3, 1-A-4, 2-A-1) and 1 sample from Virginia (3-J-2) exceeded 0.2 ppm.

The mercury levels reported in this paper could well reflect environmental conditions that are not associated with contaminated aquatic food webs or with birds feeding on mercury-treated seeds. The wide-ranging, omnivorous, terrestrial ground-feeding habits of the starling support this hypothesis. On the other hand, the residues could be a result of a short physiological retention time or could possibly be directly influenced by the season during which sample collections were made (November and December). Data illustrating the half-life of mercury residues in starlings on a whole-body basis would be helpful in interpreting these monitoring findings.

LEAD

Lead residues were found in all 23 survey samples collected. Whole body, wet-weight residues ranged from a low of 0.4 ppm at Yakima, Wash., to a high of 13.3 ppm at Chicago, Ill. The mean level for the survey was 3.18 ppm with a standard error of 0.62 ppm. When the exceptionally high reading of 13.3 ppm (almost twice as much as the next highest residue) is dropped, the mean becomes 2.70 ppm with a standard error of 0.45 ppm. Lead monitoring findings are presented in Table 3.

Little is known about environmental dispersal of lead or about its assimilation by wildlife other than that reported as a result of ingestion of shotgun pellets by

TABLE 2.—*Mercury residues in starlings, 1970*

| Sampling Site Number | Mercury Residue [1] (ppm) | Sampling Site Number | Mercury Residue [1] (ppm) | Sampling Site Number | Mercury Residue [1] (ppm) | Sampling Site Number | Mercury Residue [1] (ppm) |
|---|---|---|---|---|---|---|---|
| 1-A-1 | 0.05 | 3-D-1 | 0.05 | 4-G-1 | <0.05 | 3-I-1 | <0.05 |
| 2 | 0.06 | 2 | <0.05 | 2 | <0.05 | 2 | 0.05 |
| 3 | 1.50 | 3 | <0.05 | 3 | <0.05 | 3 | <0.05 |
| 4 | 1.90 | 4 | <0.05 | 4 | 0.10 | 4 | 0.08 |
| *Mean* | 0.878 | *Mean* | <0.05 | *Mean* | <0.062 | *Mean* | <0.058 |
| *SE* | 0.417 | *SE* | | *SE* | <0.011 | *SE* | <0.007 |
| 2-A-1 | 0.05 | 4-D-1 | 0.08 | 1-H-1 | 0.05 | 4-I-1 | <0.05 |
| 2 | <0.05 | 2 | — | 2 | 0.06 | 2 | <0.05 |
| 3 | 0.07 | 3 | <0.05 | *Mean* | 0.055 | 3 | <0.05 |
| 4 | 0.11 | *Mean* | <0.065 | *SE* | 0.067 | *Mean* | <0.050 |
| *Mean* | <0.175 | *SE* | <0.010 | | | *SE* | |
| *SE* | <0.085 | | | 2-H-1 | 0.05 | | |
| | | 1-E-1 | <0.05 | 2 | 0.07 | 5-I-1 | <0.05 |
| 3-A-1 | <0.05 | 2 | — | 3 | 0.19 | 2 | <0.05 |
| 2 | 0.07 | 3 | 0.05 | 4 | 0.05 | *Mean* | <0.050 |
| 3 | <0.05 | 4 | <0.05 | *Mean* | <0.090 | *SE* | <0.008 |
| *Mean* | <0.057 | *Mean* | <0.050 | *SE* | <0.029 | | |
| *SE* | <0.018 | *SE* | | | | 2-J-1 | 0.10 |
| | | | | 3-H-1 | <0.05 | 2 | 0.10 |
| 1-B-1 | 0.05 | 2-E-1 | 0.10 | 2 | <0.05 | 3 | 0.10 |
| 2 | 0.07 | 2 | 0.07 | 3 | 0.05 | 4 | 0.06 |
| 3 | 0.06 | 3 | 0.05 | 4 | 0.10 | *Mean* | 0.090 |
| 4 | 0.14 | 4 | <0.05 | *Mean* | 0.062 | *SE* | 0.008 |
| *Mean* | 0.080 | *Mean* | <0.068 | *SE* | <0.011 | | |
| *SE* | 0.023 | *SE* | <0.010 | | | 3-J-1 | <0.05 |
| | | | | 4-H-1 | <0.05 | 2 | 0.22 |
| 2-B-1 | 0.05 | 3-E-1 | 0.15 | 2 | 0.08 | 3 | 0.18 |
| 2 | 0.10 | 2 | <0.05 | 3 | <0.05 | *Mean* | <0.150 |
| 3 | 0.11 | 3 | <0.05 | 4 | <0.05 | *SE* | <0.053 |
| 4 | 0.06 | 4 | 0.08 | *Mean* | 0.058 | | |
| *Mean* | 0.080 | *Mean* | <0.083 | *SE* | 0.007 | 1-K-1 | 0.05 |
| *SE* | 0.016 | *SE* | <0.020 | | | 2 | 0.05 |
| | | | | 2-I-1 [2] | 0.08 | *Mean* | 0.050 |
| 3-B-1 | 0.08 | 1-F-1 | 0.11 | 2 | 0.11 | *SE* | |
| 2 | 0.09 | 2 | <0.05 | 3 | <0.05 | | |
| 3 | 0.06 | 3 | 0.05 | *Mean* | <0.080 | 2-K-1 | 0.10 |
| 4 | 0.08 | 4 | <0.05 | *SE* | <0.014 | 2 | 0.05 |
| *Mean* | 0.078 | *Mean* | 0.065 | | | *Mean* | 0.075 |
| *SE* | 0.055 | *SE* | 0.013 | | | *SE* | 0.019 |
| 4-B-1 | 0.09 | 2-F-1 | <0.05 | | | | |
| *Mean* | 0.090 | 2 | <0.05 | | | | |
| *SE* | | 3 | <0.05 | | | | |
| | | 4 | 0.18 | | | | |
| 1-C-1 [2] | 0.06 | *Mean* | 0.083 | | | | |
| 2 | — | *SE* | 0.028 | | | | |
| 3 | — | | | | | | |
| 4 [3] | <0.05 | 3-F-1 | 0.13 | | | | |
| *Mean* | <0.060 | 2 | 0.15 | | | | |
| *SE* | <0.007 | 3 | 0.13 | | | | |
| | | 4 | 0.09 | | | | |
| 2-C-1 [4] | 0.09 | *Mean* | 0.125 | | | | |
| 2 | — | *SE* | 0.010 | | | | |
| 3 | <0.05 | | | | | | |
| 4 | 0.06 | 4-F-1 | — | | | | |
| *Mean* | <0.067 | 2 | — | | | | |
| *SE* | <0.009 | 3 | 0.08 | | | | |
| | | 4 | <0.05 | | | | |
| 3-C-1 | 0.08 | *Mean* | 0.065 | | | | |
| 2 | — | *SE* | 0.010 | | | | |
| 3 [5] | <0.05 | | | | | | |
| 4 | <0.05 | | | | | | |
| *Mean* | 0.060 | | | | | | |
| *SE* | 0.008 | 1-G-1 | <0.05 | | | | |
| | | 2 | 0.05 | | | | |
| 4-C-1 | <0.05 | 3 | <0.05 | | | | |
| 2 | <0.05 | 4 | 0.05 | | | | |
| *Mean* | <0.050 | *Mean* | <0.050 | | | | |
| *SE* | | *SE* | | | | | |
| 1-D-1 [2] | 0.08 | 2-G-1 | <0.05 | | | | |
| 2 | 0.05 | 2 | <0.05 | | | | |
| 3 | <0.05 | 3 | <0.05 | | | | |
| 4 | <0.05 | 4 | <0.05 | | | | |
| *Mean* | <0.058 | *Mean* | <0.050 | | | | |
| *SE* | <0.006 | *SE* | | | | | |
| 2-D-1 | <0.05 | 3-G-1 | 0.05 | | | | |
| 2 | 0.06 | 2 | <0.05 | | | | |
| 3 | — | 3 | 0.05 | | | | |
| 4 | <0.05 | 4 | <0.05 | | | | |
| *Mean* | 0.053 | *Mean* | 0.050 | | | | |
| *SE* | <0.003 | *SE* | | | | | |

NOTE: — = no sample taken.

[1] Parts per million whole body, wet-weight basis.

[2] 2 birds.

[3] 7 birds.

[4] 8 birds.

[5] 14 birds.

waterfowl and certain game birds. Available information indicates that contamination of vegetation may be directly related to the proximity of lead pollution levels in air (*6*).

Bagley and Locke (*7*) reported occurrence of lead residues in the liver and tibia of birds that were free of lead shot in the gizzards at necropsy. These birds had been pen raised, shot, or found dead. Sampled species associated with aquatic environments contained average lead residues in the liver of from 0.5 to 2.0 ppm on a wet-weight basis. Residues in the liver of terrestrial feeding birds averaged 3.7 ppm for cowbirds (*Molothrus ater*), 3.3 ppm for mourning doves (*Zenaidura macroura*), 2.1 ppm for rock ptarmigan (*Lagopus mutus*), and 0.5 ppm for ring-necked pheasant (*Phasianus colchicus*). Lead was found in the tibia of selected aquatic birds in the order of 2 ppm to 13 ppm. The rock ptarmigan averaged 7.1 ppm of lead in the tibia, and a single dusky grouse (*Dendragapus obscurus*) was reported to have 3.0 ppm tibia lead residues. These data appear to be consistent with the survey sample findings.

TABLE 3.—*Lead residues in starlings*

| Sampling Site Number | Location | Lead Residue [1] (ppm) |
|---|---|---|
| 1 | Yakima, Wash. | 0.4 |
| 2 | Corvallis, Oreg. | 0.8 |
| 3 | Los Angeles, Calif. | |
| 4 | Reno, Nev. | 1.2 |
| 5 | Boise, Idaho | 1.6 |
| 6 | Salt Lake City, Utah | 1.5 |
| 7 | Phoenix, Ariz. | 2.1 |
| 8 | Greeley, Colo. | 1.1 |
| 9 | Carlsbad, N. Mex. | |
| 10 | Tishomingo, Okla. | 1.7 |
| 11 | Mitchell, S. Dak. | 1.5 |
| 12 | Twin Cities, Minn. | 2.9 |
| 13 | Chicago, Ill. | 13.3 |
| 14 | Sandusky, Ohio | .9 |
| 15 | Columbus, Ohio | 1.2 |
| 16 | Stuttgart, Ark. | 2.0 |
| 17 | Baton Rouge, La. | 0.8 |
| 18 | Nashville, Tenn. | 2.6 |
| 19 | Atlanta, Ga. | 4.9 |
| 20 | Gainesville, Fla. | 1.2 |
| 21 | Raleigh, N. C. | 5.2 |
| 22 | Patuxent, Md. | 3.6 |
| 23 | N. Brunswick, N. J. | 7.3 |
| 24 | Jamestown, N. Y. | 7.0 |
| 25 | Gray, Maine | 2.4 |

NOTE: Mean = 3.18.
Standard Error = .621.
Standard Deviation = 2.98.
Blank indicates no sample obtained.
[1] Parts per million whole body, wet-weight basis.


## *Acknowledgment*

Collections were made by field personnel of the Wildlife Services Division, Bureau of Sport Fisheries and Wildlife. Regional Pesticide Specialists of the Division of Wildlife Services were responsible for coordinating and reporting collections and assuring that samples were received by the contracting laboratory in proper condition. The Regional Pesticide Specialists are:

| | |
|---|---|
| James B. Elder | Minneapolis, Minn |
| Robert H. Hillen | Albuquerque, N. Mex. |
| David J. Lenhart | Portland, Oreg. |
| John C. Oberheu | Atlanta, Ga. |
| John W. Peterson | Boston, Mass. |

Paul R. Nickerson, Division of Wildlife Services, did the statstical computations and assisted in collating the data presented in this report.


See Appendix for chemical names of compounds discussed in this paper.

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# *Organochlorine Residues in Starlings—1970* [1]

William E. Martin and Paul R. Nickerson

ABSTRACT

*As part of the National Pesticide Monitoring Program, starlings were collected in November and December 1970 from 125 sites throughout the contiguous United States and analyzed for certain persistent organochlorine insecticides. DDT and its metabolites, dieldrin, heptachlor epoxide, and benzene hexachloride were found in all samples. Polychlorinated biphenyls, which were estimated using Aroclor 1254 as a standard, were also found in all samples. A comparison of 1970 residue data with baseline information from 1967-68 indicates an apparent decline in levels of DDT and its metabolites and dieldrin; however, the decline is not significant at the 95% confidence level.*

## *Introduction*

As outlined in the recent description of the national pesticide monitoring program for wildlife (*1*), a nationwide sample of starlings (*Sturnus vulgaris*) is collected every other year and analyzed to help measure environmental levels of persistent organochlorine insecticides. Baseline data for residues of these contaminants, as reported by Martin in 1969 (*2*), were developed through the analysis of three complete random sample collections taken from 1967 through 1968. This paper presents data from the 1970 collections and compares it to the baseline findings.

## *Sample Design and Collection*

The random sampling design used for this study is described by Dustman *et al.* (*1*). Basically, the design consists of 40 blocks of 5 degrees latitude (24°-49°) and longitude (64°-124°), with up to four sites randomly selected from each block. Fig. 1 shows the locations of the sampling sites, and Table 1 lists the locations sampled during the November/December 1970 collection. Sampling locations are identified by a row number, a column letter, and a site number; e.g., the site near Tacoma, Wash., is designated 1-A-1. Collections were made at 125 of the possible 139 sampling locations (90%).

Starlings again proved difficult to collect in some areas. Sampling sites in Texas presented the greatest collection problem, with no samples being taken at seven of the nine preselected locations. Since the area in question is one of high pesticide use, new collection techniques will be developed or an alternate representative species will be selected prior to the 1972 collection.

There is no specific information, other than general observation, concerning starling population variation from block to block. The sampling design takes into account the fact that differences in number of birds do occur between and within the blocks. The study, however, is designed to measure trends of environmental residues rather than effects on starling populations.

The sample from each site normally consisted of a "pool" of birds. Pools containing fewer than 10 birds are indicated by footnote in the appropriate tables. Birds collected for organochlorine residue determination were either trapped or shot. Each 10-bird pool was wrapped in aluminum foil, placed in polyethylene bags, and frozen immediately for later laboratory analyses.

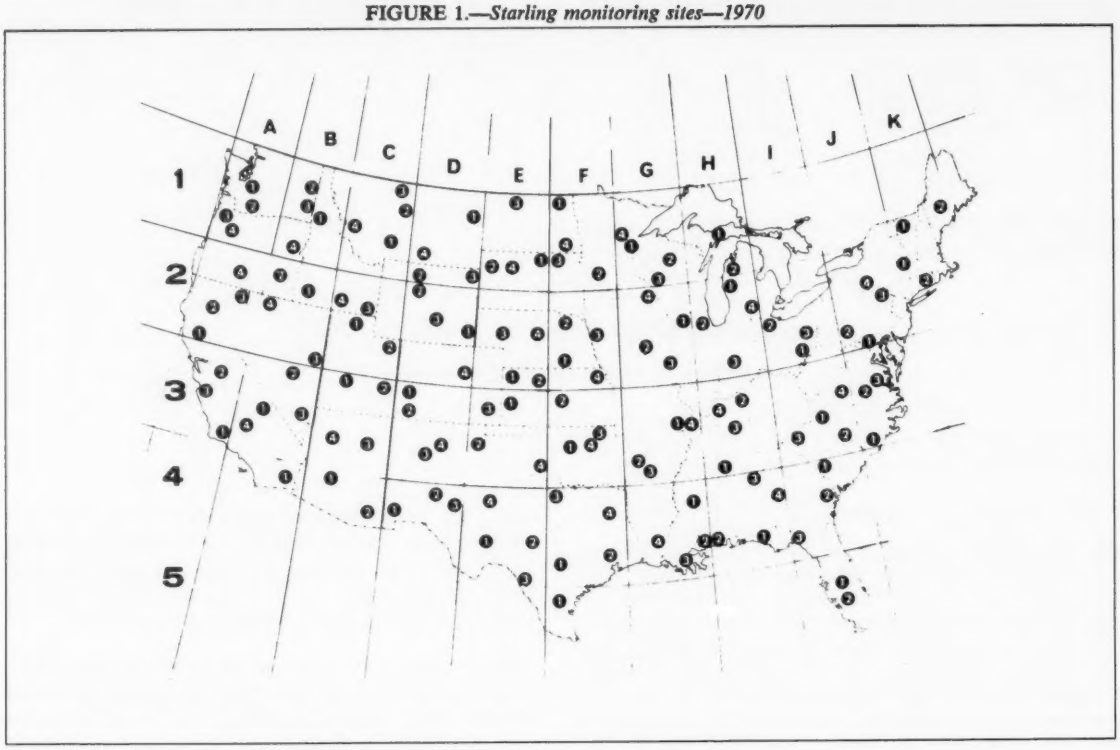
## *Sample Preparation and Analytical Methods*

Residue analyses were done by the Wisconsin Alumni Research Foundation [2] under contract with the Bureau of Sport Fisheries and Wildlife. Birds were prepared by skinning and removing the beak and wings at the first

[1] From the Branch of Pesticide Appraisal and Monitoring, Division of Wildlife Services, Bureau of Sport Fisheries and Wildlife, U. S. Department of the Interior, Washington, D. C. 20240.

[2] Mention of this commercial laboratory is for identification only and does not constitute endorsement by the U. S. Department of the Interior.

FIGURE 1.—*Starling monitoring sites—1970*




joint out from the body; the removed parts were discarded. Each 10-bird pool was ground together in a Hobart food chopper and a subsample taken for analysis.

Every effort was made to use essentially the same procedures for preparation and analyses of samples as in the baseline re: :t (*2*). Determination was made using two columns with a Barber-Coleman Pesticide Analyzer, Model 5360. Normal instrument conditions were:

| | | |
|---|---|---|
| Column: | Glass, 4 ft x 4 mm, packed with 5% DC-200 on 80/100 Gas Chrom Q | |
| Temperatures: | Injector | 230° C |
| | Column | 195° C |
| | Detector | 250° C |
| Carrier gas: | Nitrogen | |
| Flow rate: | Such that *p,p'*-DDT had a retention time of 6 to 8 minutes | |

Modifications of techniques were used for a greater degree of accuracy and discrimination in identifying the isomers (alpha, beta, delta, and gamma) of benzene hexachloride. For this determination, the column was packed with 3% OV-17 rather 5% DC-200, and appropriate instrument changes were made as follows:

| | | |
|---|---|---|
| Column: | Glass, 4 ft x 4 mm, packed with 3% OV-17 on 80/100 Gas Chrom Q | |
| Temperatures: | Injector | 230° C |
| | Column | 180° C |
| | Detector | 240° C |
| Flow rate: | Such that gamma BHC has a retention time of 2 minutes | |

Polychlorinated biphenyls (PCB's) were estimated by using the peaks between DDD and DDT on the DC-200 column with Aroclor 1254 as a standard. On the basis of the findings of Risebrough, Reiche, and Olcott (*3*) regarding the lack of significant PCB interference with analytical findings for *p,p'*-DDE and because of a tight budgetary allowance for starling monitoring efforts, the PCB question was not pursued. However, it is expected that a closer analytical scrutiny would reveal PCB's other than the Aroclor 1254 estimates. The PCB estimates are provided only to help place in context the readings for DDT and DDD and to demonstrate the common occurrence of PCB's in starling tissues.

The residue data were not corrected for recovery. The standardized analytical procedure results in an 88% to 105% recovery rate for the chemicals reported in this paper. Recovery and confirmatory tests were done internally by the commercial laboratory on a quality control basis. Limits of detection ranged from 0.005 ppm to 0.01 ppm.

TABLE 1.—*Starling sampling site locations by State and county, 1970*

| State | Sampling Site Number | County |
|---|---|---|
| Alabama | 3-H-1 | Marion |
| | 4-H-3 | Talladega |
| Arizona | 3-C-3 | Navajo |
| | 3-C-4 | Yavapi |
| | 4-C-1 | Maricopa |
| | 4-C-2 | Graham |
| Arkansas | 3-G-2 | Yell/Pope |
| | 3-G-3 | Lonoke/Pulaski |
| California | 2-A-1 | Colusa |
| | 2-A-2 | Shasta |
| | 2-A-3 | Modoc |
| | 3-A-1 | Ventura |
| | 3-A-2 | Stanislaus |
| | 3-A-3 | Monterey |
| | 3-B-1 | Inyo |
| | 3-B-4 | Kern |
| | 4-B-1 | Imperial |
| Colorado | 2-D-4 | Adams |
| | 3-D-1 | Montrose |
| | 3-D-2 | La Plata/Rio Grande |
| | 3-E-3 | Otero |
| Connecticut | 2-K-2 | New London |
| Florida | 4-H-1 | Bay |
| | 4-I-3 | Madison |
| | 5-I-1 | Polk |
| | 5-I-2 | Hardee |
| Georgia | 4-H-4 | Pike |
| | 4-I-2 | Wayne |
| Idaho | 1-B-1 | Nezperce |
| | 2-B-1 | Owyhee |
| | 2-C-3 | Franklin |
| | 2-C-4 | Minidoka |
| Illinois | 2-G-1 | Stephencon |
| | 2-G-3 | Sangamon |
| | 2-H-2 | Cook |
| Indiana | 2-H-3 | Henry |
| Iowa | 2-F-3 | Pottawattamie |
| | 2-G-2 | Polk |
| | 2-G-4 | Butler |
| Kansas | 2-E-1 | Rawlins |
| | 2-E-2 | Smith |
| | 3-E-1 | Hamilton/Kearny |
| | 2-F-4 | Nemaha |
| | 3-F-2 | Marion |
| Kentucky | 3-H-2 | Ohio |
| | 3-H-4 | Hopkins |
| Louisiana | 4-G-3 | Jefferson |
| | 4-G-4 | Rapides |
| Maine | 1-K-2 | Penobscot |
| Maryland | 2-J-1 | Prince Georges |
| Michigan | 1-H-1 | Chippewa |
| | 1-H-2 | Grand Traverse |
| | 2-H-1 | Kent |
| | 2-H-4 | Inaham |
| Minnesota | 1-F-2 | Swift |
| | 1-G-1 | Pine |
| | 1-G-4 | Aitkin |
| Mississippi | 4-G-1 | Leake |
| | 4-G-2 | Harrison |
| | 4-H-2 | Jackson |
| Missouri | 3-G-1 | Stoddard |
| | 3-G-4 | Bollinger |
| Montana | 1-C-1 | Meagher |
| | 1-C-4 | Missoula |
| | 1-D-1 | Richland |
| | 1-D-4 | Yellowstone |
| Nebraska | 2-E-3 | Keith |
| | 2-E-4 | Lincoln |
| | 2-F-1 | Clay |
| | 2-F-2 | Antelope |
| Nevada | 2-B-3 | White Pine |
| | 2-B-4 | Humboldt |
| | 3-B-2 | Nye |
| | 3-B-3 | Clark |
| New Mexico | 3-D-3 | Bernalillo |
| | 3-D-4 | Santa Fe/Torrance |
| | 4-D-1 | Luna |
| | 4-D-3 | Chaves |
| | 3-E-2 | Quay |
| New York | 2-J-4 | Oswego |
| | 2-K-1 | Rennselaer |
| North Carolina | 3-I-1 | Wilkes |
| | 3-I-2 | Union |
| | 3-I-3 | Macon |
| | 3-J-1 | Pender |
| North Dakota | 1-E-3 | Ward |
| | 1-F-1 | Cavelier |
| | 1-F-4 | Dickey |
| Ohio | 2-I-1 | Washington |
| | 2-I-2 | Erie |
| | 2-I-3 | Jefferson |
| Oklahoma | 3-E-4 | Greer |
| | 3-F-1 | Canadian |
| | 3-F-3 | Nowata |
| | 3-F-4 | Okmulgee |
| Oregon | 1-A-3 | Yamhill |
| | 1-A-4 | Lane |
| | 2-A-4 | Klamath |
| | 1-B-4 | Baker |
| | 2-B-2 | Harney |
| Pennsylvania | 2-J-2 | Somerset |
| | 2-J-3 | Cuzerne |
| South Carolina | 4-I-1 | Aiken |
| South Dakota | 1-E-1 | Potter |
| | 1-E-4 | Hughes |
| | 1-F-3 | Brown |
| Tennessee | 3-H-3 | Davidson |
| Texas | 4-F-3 | Clay |
| | 4-F-4 | Morris |
| Utah | 2-C-1 | Weber |
| | 3-C-1 | Sevier/Millard |
| Vermont | 1-K-1 | Addison |
| Virginia | 3-I-4 | Amherst |
| | 3-J-2 | Prince George |
| | 3-J-3 | Caroline |
| Washington | 1-A-1 | Pierce |
| | 1-A-2 | Yakima |
| | 1-B-2 | Spokane |
| | 1-B-3 | Whitman |
| Wisconsin | 1-G-2 | Curtiss |
| | 1-G-3 | Trempeleau |
| Wyoming | 1-D-2 | Big Horn |
| | 1-D-3 | Brook |
| | 2-D-1 | Goshen |
| | 2-D-2 | Washakie |

Total sites = 125

## *Results and Discussion*

Residue levels of organochlorine insecticides and PCB's for the November/December 1970 collection are presented in Table 7. The sampling design used in this study was chosen primarily because it permitted statistical comparison of the distribution of pesticide residues on a nationwide basis. The arbitrarily selected 5-degree blocks are the basic units for evaluating nationwide trends. Comparison of the distribution of average residues by frequency of occurrence in different quantitative ranges for the 1967-68 and 1970 collections (Table 4) offers an additional tool for evaluating changes in residue levels.

### DDT AND METABOLITES

As in 1967-68, DDT and its metabolites were found in all samples taken. The 1970 block averages appear to reflect a general nationwide decline in levels, although this is only apparent and is not significant at the 95% confidence level (Table 2).

TABLE 2.—*Block averages of residues of DDT and its metabolites*

| | Baseline Data 1967-68 | | Fall 1970 | |
|---|---|---|---|---|
| Sampling Block | Average Residue Level (ppm) | Standard Error | Average Residue Level (ppm) | Standard Error |
| 1A | 1.734 | .350 | .775 | .260 |
| 2A | .755 | .167 | .472 | .093 |
| 3A | 2.281 | .318 | 1.779 | .768 |
| 1B | .809 | 1.320 | .345 | .064 |
| 2B | 1.070 | .331 | .975 | .400 |
| 3B | 1.767 | .590 | 1.053 | .519 |
| 4B | 3.450 | 1.490 | 2.192 | — |
| 1C | .341 | .120 | .145 | .002 |
| 2C | 3.616 | 2.190 | .373 | .088 |
| 3C | 1.988 | .651 | .470 | .152 |
| 4C | 12.966 | 4.511 | 7.903 | 4.930 |
| 1D | .159 | .038 | .106 | .017 |
| 2D | .432 | .104 | .263 | .078 |
| 3D | 1.162 | .237 | .502 | .069 |
| 4D | 12.574 | 8.155 | 3.130 | 1.160 |
| 1E | .919 | .433 | .099 | .010 |
| 2E | .342 | .065 | .256 | .051 |
| 3E | 1.736 | .706 | 1.460 | 1.114 |
| 1F | .219 | .044 | .244 | .098 |
| 2F | .297 | .050 | .171 | .032 |
| 3F | .713 | .144 | .229 | .065 |
| 4F | .667 | — | .172 | .007 |
| 1G | .305 | .064 | .178 | .023 |
| 2G | .443 | .080 | .266 | .023 |
| 3G | 2.134 | .870 | 1.822 | 1.008 |
| 4G | 4.201 | .996 | 2.449 | .877 |
| 1H | 1.012 | .312 | .231 | .042 |
| 2H | 1.089 | .182 | 1.213 | .402 |
| 3H | 1.463 | .553 | .937 | .446 |
| 4H | 2.110 | .423 | 2.135 | .425 |
| 2I | .576 | .209 | .455 | .155 |
| 3I | .673 | .136 | .409 | .121 |
| 4I | 4.335 | .812 | 2.619 | .706 |
| 5I | 1.550 | .299 | .316 | .117 |
| 2J | .689 | .102 | .716 | .321 |
| 3J | .795 | .211 | .709 | .136 |
| 1K | .364 | .053 | .303 | .077 |
| 2K | .593 | .081 | .411 | .068 |

Individual sites having DDT and metabolite residues greater than 3.0 ppm in baseline and/or 1970 data are listed in Table 3, and frequency of occurrence of residues in different quantitative ranges is shown in Table 4. Sites containing the highest DDT and metabolite levels continue to be found in southern Arizona and New Mexico and in areas of the Southeast, including parts of Florida, Georgia, Alabama, Mississippi, Louisiana, and Arkansas. Because starlings were not available, we do not have 1970 data for two sites in Utah that had high residue levels in the baseline collections. Other States yielding relatively high residue levels (greater than 3.0 ppm) at one or more sites include Oklahoma, California, and South Carolina.

### DIELDRIN

As with DDT, dieldrin residue levels are apparently declining from the baseline findings, although again the decline is not significant at the 95% confidence level (Table 5). Two exceptionally high residue levels of 3.59 and 1.52 ppm were found, however, along the upper Mississippi River drainage area (Sites 2-G-3 and 2-G-4). States from which samples were obtained with relatively high residue levels (greater than 0.3 ppm) at one or more sites include Georgia, Illinois, Iowa, Kansas, Missouri, and Washington. Individual sites having dieldrin residue levels greater than 0.3 ppm in baseline and/or 1970 collections are listed in Table 6, and frequency of occurrence of residues in different quantitative ranges is shown in Table 4.

### BHC

BHC was found in all 125 samples collected in 1970; whereas, in the 1967-68 baseline study of three collections (375 samples), it was found in only 45 samples. The lindane reported in 105 samples of the baseline study is thought to have resulted as a product of technical BHC (Table 7).

BHC figures presented for 1970 cannot be related directly to the 1967-68 baseline figures, and it was decided not to re-analyze the 1967-68 baseline samples with the new techniques at this time because the levels were relatively low compared to established tolerances for edible food and feed.

### HEPTACHLOR EPOXIDE

Heptachlor epoxide was found in all samples collected in 1970 (Table 7) and in 168 of 375 samples in the 1967-68 baseline study. Although the frequency of occurrence of heptachlor epoxide was greater for the 1970 collection, there is no statistically significant difference between the residue levels found in the 1970 sample and the baseline data. Any attempt at describing a trend in heptachlor epoxide residue levels in starlings should

be delayed until after residue levels for the 1972 collections are determined. Improvements in analytical methodology may be partly responsible for the apparent increase in frequency of occurrence of heptachlor epoxide residues.

TABLE 3.—*Sites with residue levels of DDT and its metabolites greater than 3.0 ppm in baseline and/or 1970 collections*

| Sampling Site Number | DDT Residues in ppm | |
|---|---|---|
| | Baseline Data 1967-68 | 1970 |
| 3-A-1 | 1.903 | 3.660 |
| 3-B-4 | 4.376 | 2.837 |
| 2-C-2 | 9.551 | no sample |
| 3-C-2 | 3.163 | no sample |
| 4-C-1 | 23.902 | 14.874 |
| 4-D-1 | 1.930 | 4.780 |
| 4-D-3 | 19.680 | 1.479 |
| 3-E-4 | 4.948 | 5.318 |
| 3-G-3 | 5.950 | 5.313 |
| 4-G-1 | 8.128 | 3.413 |
| 4-G-2 | 1.580 | 4.801 |
| 4-G-4 | 4.220 | 1.210 |
| 4-H-3 | 2.347 | 3.060 |
| 4-H-4 | 3.510 | 2.546 |
| 4-I-1 | 5.483 | 3.026 |
| 4-I-3 | 5.668 | 3.872 |

TABLE 4.—*Distribution of average residues of DDT and its metabolites and dieldrin by frequency of occurrence in different quantitative ranges—1967-68 and 1970 collections*

| Residue Range (ppm) | Frequency of Occurrence (Sites) | |
|---|---|---|
| | 1967-68 | 1970 |
| DDT AND METABOLITES | | |
| ≤1.0 | 76 | 103 |
| >1.0 and ≤2.0 | 25 | 5 |
| >2.0 and ≤3.0 | 12 | 7 |
| >3.0 and ≤4.0 | 3 | 5 |
| >4.0 and ≤5.0 | 3 | 2 |
| >5.0 and ≤10.0 | 5 | 2 |
| >10.0 and ≤15.0 | 0 | 1 |
| >15.0 and ≤20.0 | 1 | — |
| >20.0 and ≤25.0 | 1 | — |
| Total sites | 126 | 125 |
| DIELDRIN | | |
| ≤0.1 | 65 | 98 |
| >0.1 and ≤0.2 | 40 | 12 |
| >0.2 and ≤0.3 | 11 | 6 |
| >0.3 and ≤0.4 | 2 | 2 |
| >0.4 and ≤0.5 | 3 | 1 |
| >0.5 and ≤1.0 | 4 | 4 |
| >1.0 and ≤1.5 | 1 | 1 |
| >1.5 and ≤2.0 | — | — |
| >2.0 and ≤2.5 | — | — |
| >2.5 | — | 1 |
| Total sites | 126 | 125 |

TABLE 5.—*Block averages of dieldrin residues*

| Sampling Block | Baseline Data 1967-68 | | Fall 1970 | |
|---|---|---|---|---|
| | Average Residue Level (ppm) | Standard Error | Average Residue Level (ppm) | Standard Error |
| 1A | .339 | .094 | .129 | .019 |
| 2A | .066 | .031 | .020 | .005 |
| 3A | .074 | .016 | .041 | .008 |
| 1B | .339 | .120 | .237 | .116 |
| 2B | .073 | .019 | .023 | .005 |
| 3B | .128 | .029 | .030 | .005 |
| 4B | .167 | .061 | .026 | — |
| 1C | .062 | .025 | .005 | — |
| 2C | .021 | .030 | .015 | .007 |
| 3C | .102 | .029 | .035 | .012 |
| 4C | .069 | .018 | .014 | .007 |
| 1D | .028 | .010 | .012 | .005 |
| 2D | .089 | .028 | .005 | — |
| 3D | .107 | .037 | .021 | .005 |
| 4D | .041 | .009 | .088 | .058 |
| 1E | .093 | .040 | .009 | .001 |
| 2E | .143 | .049 | .095 | .034 |
| 3E | .095 | .019 | .124 | .086 |
| 1F | .169 | .067 | .052 | .024 |
| 2F | .123 | .033 | .093 | .060 |
| 3F | .079 | .035 | .038 | .018 |
| 4F | .034 | — | .020 | .010 |
| 1G | .094 | .040 | .065 | .023 |
| 2G | .338 | .099 | 1.458 | .665 |
| 3G | .755 | .060 | .215 | .095 |
| 4G | .297 | .119 | .061 | .017 |
| 1H | .080 | .037 | .032 | .012 |
| 2H | .127 | .043 | .162 | .068 |
| 3H | .104 | .031 | .067 | .016 |
| 4H | .142 | .035 | .120 | .047 |
| 2I | .118 | .048 | .124 | .052 |
| 3I | .360 | .233 | .020 | .005 |
| 4J | .045 | .005 | .305 | .183 |
| 5I | .073 | .023 | .018 | .007 |
| 2J | .133 | .060 | .063 | .020 |
| 3J | .120 | .078 | .072 | .036 |
| 1K | .023 | .009 | .014 | — |
| 2K | .012 | .001 | .015 | .001 |

TABLE 6.—*Sites with residue levels of dieldrin greater than 0.3 ppm in baseline and/or 1970 collections*

| Sampling Site Number | Dieldrin Residues in ppm | |
|---|---|---|
| | Baseline Data 1967-68 | 1970 |
| 1-A-3 | 0.528 | 0.160 |
| 1-A-4 | 0.492 | 0.140 |
| 1-B-3 | 0.587 | 0.600 |
| 1-B-4 | 0.418 | 0.018 |
| 3-E-1 | 0.102 | 0.420 |
| 2-G-1 | 0.280 | 0.590 |
| 2-G-3 | 0.657 | 3.590 |
| 2-G-4 | 0.032 | 1.520 |
| 3-G-1 | 0.403 | 0.230 |
| 3-G-3 | 0.317 | 0.067 |
| 3-G-4 | 0.207 | 0.520 |
| 4-G-2 | 0.970 | 0.067 |
| 2-H-2 | 0.208 | 0.330 |
| 3-I-1 | 1.385 | 0.018 |
| 4-I-2 | 0.027 | 0.750 |
| 3-J-1 | 0.333 | 0.160 |

TABLE 7.—*Pesticide residue levels in starlings, 1970*

| Sampling Site Number | Wet Weight (grams) | Lipid Weight (grams) | Residues in PPM (μg/g, wet-weight) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | DDE | DDD | DDT | DDT and Metabolites | Estimated PCB's | Dieldrin | Heptachlor Epoxide | BHC |
| 1-A-1 | 19.98 | 0.115 | 0.430 | 0.029 | 0.022 | 0.481 | 0.31 | 0.150 | 0.053 | 0.009 |
| 1-A-2 | 20.02 | 0.370 | 0.320 | 0.016 | 0.021 | 0.357 | 0.15 | 0.066 | 0.009 | 0.390 |
| 1-A-3 | 19.99 | 0.814 | 0.520 | 0.033 | 0.045 | 0.598 | 0.38 | 0.160 | 0.016 | 0.015 |
| 1-A-4 | 20.02 | 0.869 | 1.620 | 0.013 | 0.029 | 1.662 | 0.23 | 0.140 | 0.012 | 0.110 |
| 2-A-1 | 20.00 | 0.789 | 0.670 | 0.013 | 0.023 | 0.706 | 0.26 | 0.022 | 0.013 | 0.013 |
| 2-A-2 | 20.03 | 0.742 | 0.180 | 0.009 | 0.022 | 0.211 | 0.25 | 0.016 | 0.009 | 0.009 |
| 2-A-3 | 19.98 | 1.210 | 0.550 | 0.008 | 0.014 | 0.572 | 0.17 | 0.034 | 0.019 | 0.013 |
| 2-A-4 | 20.00 | 1.281 | 0.380 | 0.006 | 0.013 | 0.399 | 0.14 | 0.006 | 0.088 | 0.021 |
| 3-A-1 | 20.03 | 0.813 | 3.590 | 0.017 | 0.053 | 3.660 | 0.65 | 0.021 | 0.034 | 0.005 |
| 3-A-2 | 20.00 | 0.803 | 0.710 | 0.023 | 0.090 | 0.823 | 0.96 | 0.057 | 0.016 | 0.015 |
| 3-A-3 | 19.99 | 0.830 | 0.770 | 0.031 | 0.053 | 0.854 | 0.39 | 0.045 | 0.019 | 0.015 |
| 1-B-1 | 20.05 | 1.285 | 0.150 | 0.014 | 0.015 | 0.179 | 0.14 | 0.050 | 0.014 | 0.230 |
| 1-B-2 | 19.99 | 1.063 | 0.280 | 0.034 | 0.038 | 0.352 | 0.36 | 0.280 | 0.016 | 0.160 |
| 1-B-3 | 20.00 | 1.203 | 0.450 | 0.040 | 0.048 | 0.538 | 0.39 | 0.600 | 0.013 | 0.590 |
| 1-B-4 | 19.99 | 1.443 | 0.230 | 0.026 | 0.055 | 0.311 | 0.50 | 0.018 | 0.027 | 0.031 |
| 2-B-1 | 20.00 | 1.184 | 0.410 | 0.006 | 0.011 | 0.427 | 0.09 | 0.018 | 0.026 | 0.013 |
| 2-B-2 | 19.96 | 1.069 | 0.200 | 0.039 | 0.160 | 0.399 | 2.19 | 0.008 | 0.011 | 0.240 |
| 2-B-3 | 20.04 | 1.305 | 2.250 | 0.028 | 0.065 | 2.343 | 0.78 | 0.032 | 0.032 | 0.035 |
| 2-B-4 | 20.01 | 1.422 | 0.700 | 0.012 | 0.017 | 0.729 | 0.15 | 0.034 | 0.016 | 0.016 |
| 3-B-1 | 20.01 | 1.377 | 0.580 | 0.021 | 0.033 | 0.634 | 0.36 | 0.045 | 0.039 | 0.010 |
| 3-B-2 | 20.00 | 1.388 | 0.240 | 0.016 | 0.016 | 0.272 | 0.25 | 0.018 | 0.170 | 0.012 |
| 3-B-3 | 19.99 | 1.411 | 0.360 | 0.038 | 0.069 | 0.467 | 0.79 | 0.035 | 0.038 | 0.022 |
| 3-B-4 | 20.00 | 0.753 | 2.750 | 0.026 | 0.061 | 2.837 | 0.51 | 0.023 | 0.016 | 0.018 |
| 4-B-1 | 20.01 | 1.000 | 2.110 | 0.029 | 0.053 | 2.192 | 0.53 | 0.026 | 0.120 | 0.025 |
| 1-C-1 [1] | 20.00 | 2.454 | 0.110 | 0.015 | 0.024 | 0.149 | 0.17 | 0.005 | 0.010 | 0.031 |
| 1-C-4 [2] | 20.01 | 0.737 | 0.064 | 0.028 | 0.049 | 0.141 | 0.66 | 0.005 | 0.009 | 0.015 |
| 2-C-1 [2] | 20.07 | 0.903 | 0.140 | 0.005 | 0.012 | 0.157 | 0.13 | 0.008 | 0.026 | 0.013 |
| 2-C-3 | 19.98 | 0.924 | 0.480 | 0.006 | 0.013 | 0.499 | 0.14 | 0.031 | 0.039 | 0.014 |
| 2-C-4 | 20.06 | 1.303 | 0.420 | 0.019 | 0.024 | 0.463 | 0.25 | 0.005 | 0.017 | 0.036 |
| 3-C-1 | 19.99 | 1.479 | 0.750 | 0.021 | 0.044 | 0.815 | 0.27 | 0.039 | 0.022 | 0.013 |
| 3-C-3 [2] | 20.01 | 0.969 | 0.350 | 0.022 | 0.047 | 0.419 | 0.36 | 0.008 | 0.010 | 0.007 |
| 3-C-4 | 19.98 | 0.777 | 0.150 | 0.009 | 0.017 | 0.176 | 0.15 | 0.057 | 0.012 | 0.008 |
| 4-C-1 | 20.06 | 0.924 | 14.800 | 0.036 | 0.038 | 14.874 | 0.32 | 0.005 | 0.007 | 0.034 |
| 4-C-2 | 20.10 | 0.638 | 0.870 | 0.022 | 0.040 | 0.932 | 0.31 | 0.022 | 0.015 | 0.008 |
| 1-D-1 [2] | 20.00 | 0.978 | 0.078 | 0.005 | 0.005 | 0.088 | 0.05 | 0.005 | 0.006 | 0.016 |
| 1-D-2 | 19.97 | 0.860 | 0.050 | 0.014 | 0.025 | 0.089 | 0.29 | 0.029 | 0.015 | 0.005 |
| 1-D-3 | 20.03 | 2.397 | 0.094 | 0.011 | 0.017 | 0.122 | 0.17 | 0.007 | 0.080 | 0.017 |
| 1-D-4 | 19.99 | 1.045 | 0.064 | 0.025 | 0.034 | 0.123 | 0.30 | 0.008 | 0.010 | 0.014 |
| 2-D-1 [2] | 20.03 | 1.025 | 0.310 | 0.005 | 0.010 | 0.325 | 0.14 | 0.005 | 0.006 | 0.160 |
| 2-D-2 | 19.98 | 0.704 | 0.047 | 0.008 | 0.022 | 0.077 | 0.19 | 0.005 | 0.011 | 0.019 |
| 2-D-4 | 20.04 | 1.355 | 0.350 | 0.016 | 0.022 | 0.388 | 0.14 | 0.005 | 0.019 | 0.022 |
| 3-D-1 | 19.99 | 1.323 | 0.790 | 0.015 | 0.028 | 0.733 | 0.29 | 0.031 | 0.019 | 0.012 |
| 3-D-2 | 20.00 | 1.554 | 0.380 | 0.014 | 0.029 | 0.423 | 0.20 | 0.018 | 0.009 | 0.045 |
| 3-D-3 | 20.02 | 1.181 | 0.340 | 0.007 | 0.035 | 0.382 | 0.72 | 0.019 | 0.012 | 0.009 |
| 3-D-4 | 19.99 | 0.839 | 0.430 | 0.014 | 0.026 | 0.470 | 0.20 | 0.016 | 0.008 | 0.012 |
| 4-D-1 | 19.90 | 0.735 | 4.750 | 0.013 | 0.017 | 4.780 | 0.17 | 0.170 | 0.026 | 0.012 |
| 4-D-3 | 19.99 | 1.156 | 1.450 | 0.009 | 0.020 | 1.479 | 0.25 | 0.006 | 0.006 | 0.016 |
| 1-E-1 | 20.06 | 1.385 | 0.062 | 0.014 | 0.023 | 0.099 | 0.26 | 0.005 | 0.006 | 0.013 |
| 1-E-3 | 20.02 | 0.976 | 0.071 | 0.017 | 0.032 | 0.120 | 0.37 | 0.008 | 0.009 | 0.011 |
| 1-E-4 | 20.00 | 1.400 | 0.056 | 0.010 | 0.013 | 0.079 | 0.11 | 0.013 | 0.024 | 0.014 |
| 2-E-1 | 20.02 | 1.069 | 0.130 | 0.028 | 0.044 | 0.202 | 0.41 | 0.21 | 0.015 | 0.017 |
| 2-E-2 | 20.01 | 0.943 | 0.082 | 0.030 | 0.034 | 0.146 | 0.29 | 0.041 | 0.009 | 0.010 |
| 2-E-3 | 20.00 | 1.561 | 0.320 | 0.043 | 0.055 | 0.418 | 0.47 | 0.044 | 0.016 | 0.014 |
| 2-E-4 | 19.99 | 1.518 | 0.200 | 0.017 | 0.039 | 0.256 | 0.38 | 0.086 | 0.120 | 0.023 |
| 3-E-1 | 20.00 | 1.176 | 0.140 | 0.005 | 0.006 | 0.151 | 0.09 | 0.420 | 0.017 | 0.012 |
| 3-E-2 | 19.93 | 0.739 | 0.190 | 0.019 | 0.049 | 0.258 | 0.36 | 0.026 | 0.012 | 0.010 |
| 3-E-3 | 19.99 | 1.018 | 0.099 | 0.006 | 0.009 | 0.114 | 0.17 | 0.014 | 0.008 | 0.008 |
| 3-E-4 | 20.09 | 0.794 | 5.290 | 0.011 | 0.117 | 5.318 | 0.12 | 0.034 | 0.010 | 0.008 |
| 1-F-1 | 19.99 | 1.639 | 0.015 | 0.016 | 0.019 | 0.050 | 0.14 | 0.021 | 0.015 | 0.018 |
| 1-F-2 | 20.00 | 1.639 | 0.110 | 0.044 | 0.063 | 0.217 | 0.58 | 0.048 | 0.100 | 0.017 |
| 1-F-3 | 20.01 | 1.799 | 0.520 | 0.021 | 0.028 | 0.569 | 0.19 | 0.130 | 0.019 | 0.015 |
| 1-F-4 | 20.01 | 1.521 | 0.081 | 0.017 | 0.041 | 0.139 | 0.26 | 0.007 | 0.009 | 0.016 |

TABLE 7.—*Pesticide residue levels in starlings, 1970*—Continued

| Sampling Site Number | Wet Weight (grams) | Lipid Weight (grams) | Residues in PPM (µg/g, wet-weight) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | DDE | DDD | DDT | DDT and Metabolites | Estimated PCB's | Dieldrin | Heptachlor Epoxide | BHC |
| 2-F-1 | 19.98 | 1.571 | 0.130 | 0.009 | 0.016 | 0.155 | 0.13 | 0.015 | 0.013 | 0.011 |
| 2-F-2 | 19.98 | 1.351 | 0.180 | 0.006 | 0.028 | 0.214 | 0.25 | 0.049 | 0.056 | 0.020 |
| 2-F-3 | 20.00 | 2.269 | 0.180 | 0.025 | 0.034 | 0.239 | 0.33 | 0.300 | 0.093 | 0.048 |
| 2-F-4 | 20.04 | 0.910 | 0.047 | 0.009 | 0.019 | 0.075 | 0.14 | 0.009 | 0.007 | 0.016 |
| 3-F-1 | 20.02 | 0.909 | 0.091 | 0.007 | 0.014 | 0.112 | 0.21 | 0.012 | 0.015 | 0.010 |
| 3-F-2 | 19.96 | 1.195 | 0.140 | 0.008 | 0.015 | 0.163 | 0.25 | 0.034 | 0.019 | 0.012 |
| 3-F-3 | 19.96 | 1.089 | 0.390 | 0.019 | 0.039 | 0.448 | 0.45 | 0.009 | 0.016 | 0.012 |
| 3-F-4 | 19.98 | 0.896 | 0.170 | 0.006 | 0.015 | 0.191 | 0.18 | 0.098 | 0.031 | 0.011 |
| 4-F-3 | 20.07 | 0.755 | 0.140 | 0.009 | 0.015 | 0.164 | 0.15 | 0.035 | 0.024 | 0.012 |
| 4-F-4 | 20.06 | 0.568 | 0.160 | 0.005 | 0.015 | 0.180 | 0.17 | 0.005 | 0.007 | 0.013 |
| 1-G-1 | 19.98 | 1.443 | 0.096 | 0.031 | 0.082 | 0.209 | 1.00 | 0.013 | 0.011 | 0.013 |
| 1-G-2 | 19.99 | 1.196 | 0.069 | 0.010 | 0.024 | 0.103 | 0.26 | 0.026 | 0.016 | 0.013 |
| 1-G-3 | 20.06 | 2.358 | 0.100 | 0.028 | 0.053 | 0.181 | 0.55 | 0.120 | 0.045 | 0.016 |
| 1-G-4 | 20.01 | 2.510 | 0.160 | 0.025 | 0.034 | 0.219 | 0.29 | 0.100 | 0.028 | 0.020 |
| 2-G-1 | 19.98 | 1.763 | 0.250 | 0.019 | 0.038 | 0.307 | 0.29 | 0.59 | 0.340 | 0.024 |
| 2-G-2 | 20.02 | 1.909 | 0.150 | 0.019 | 0.028 | 0.197 | 0.29 | 0.13 | 0.028 | 0.120 |
| 2-G-3 | 20.04 | 1.636 | 0.200 | 0.029 | 0.080 | 0.309 | 0.87 | 3.59 | 0.970 | 0.030 |
| 2-G-4 | 20.01 | 1.870 | 0.210 | 0.014 | 0.028 | 0.252 | 0.22 | 1.52 | 0.110 | 0.034 |
| 3-G-1 | 20.02 | 2.002 | 0.630 | 0.032 | 0.047 | 0.709 | 0.48 | 0.230 | 0.084 | 0.021 |
| 3-G-2 | 20.00 | 0.827 | 0.680 | 0.019 | 0.031 | 0.730 | 0.38 | 0.043 | 0.100 | 0.014 |
| 3-G-3 | 19.98 | 0.916 | 5.240 | 0.034 | 0.039 | 5.313 | 0.28 | 0.067 | 0.013 | 0.017 |
| 3-G-4 | 19.97 | 2.384 | 0.450 | 0.040 | 0.045 | 0.535 | 0.43 | 0.520 | 0.120 | 0.041 |
| 4-G-1 | 20.00 | 0.703 | 3.300 | 0.038 | 0.075 | 3.413 | 0.56 | 0.075 | 0.036 | 0.019 |
| 4-G-2 | 20.01 | 0.733 | 4.690 | 0.041 | 0.070 | 4.801 | 0.40 | 0.067 | 0.099 | 0.011 |
| 4-G-3 | 20.00 | 0.619 | 0.260 | 0.014 | 0.099 | 0.373 | 1.260 | 0.005 | 0.210 | 0.017 |
| 4-G-4 | 20.00 | 0.842 | 1.030 | 0.050 | 0.130 | 1.210 | 1.82 | 0.095 | 0.130 | 0.051 |
| 1-H-1 | 20.06 | 2.594 | 0.150 | 0.068 | 0.073 | 0.291 | 0.82 | 0.016 | 0.034 | 0.026 |
| 1-H-2 | 19.98 | 0.897 | 0.120 | 0.015 | 0.036 | 0.171 | 0.46 | 0.048 | 0.021 | 0.039 |
| 2-H-1 | 20.00 | 2.319 | 0.410 | 0.099 | 0.260 | 0.769 | 3.13 | 0.031 | 0.110 | 0.030 |
| 2-H-2 | 20.00 | 1.703 | 2.410 | 0.050 | 0.120 | 2.580 | 1.36 | 0.330 | 0.630 | 0.039 |
| 2-H-3 | 19.97 | 1.348 | 0.360 | 0.069 | 0.110 | 0.539 | 1.35 | 0.260 | 0.063 | 0.140 |
| 2-H-4 | 19.96 | 1.935 | 0.830 | 0.041 | 0.091 | 0.962 | 0.93 | 0.025 | 0.050 | 0.011 |
| 3-H-1 | 20.09 | 0.665 | 2.400 | 0.010 | 0.022 | 2.432 | 0.25 | 0.085 | 0.027 | 0.013 |
| 3-H-2 | 19.98 | 1.087 | 0.140 | 0.007 | 0.019 | 0.166 | 0.41 | 0.012 | 0.007 | 0.011 |
| 3-H-3 | 20.00 | 1.137 | 0.320 | 0.013 | 0.023 | 0.356 | 0.28 | 0.081 | 0.099 | 0.030 |
| 3-H-4 | 19.99 | 0.874 | 0.750 | 0.010 | 0.034 | 0.794 | 0.28 | 0.091 | 0.019 | 0.012 |
| 4-H-1 | 20.08 | 1.171 | 0.730 | 0.012 | 0.024 | 0.766 | 0.26 | 0.087 | 0.100 | 0.012 |
| 4-H-2 | 20.01 | 0.873 | 1.720 | 0.170 | 0.280 | 2.170 | 3.37 | 0.280 | 0.150 | 0.026 |
| 4-H-3 | 20.03 | 1.074 | 1.640 | 0.340 | 1.080 | 3.060 | 24.30 | 0.062 | 0.100 | 0.024 |
| 4-H-4 | 20.02 | 1.055 | 2.500 | 0.015 | 0.031 | 2.546 | 0.25 | 0.051 | 0.022 | 0.016 |
| 2-I-1 [2] | 19.98 | 2.176 | 0.410 | 0.050 | 0.079 | 0.539 | 0.80 | 0.130 | 0.056 | 0.030 |
| 2-I-2 | 20.06 | 1.192 | 0.510 | 0.055 | 0.082 | 0.647 | 0.89 | 0.230 | 0.032 | 0.017 |
| 2-I-3 | 20.05 | 1.050 | 0.110 | 0.025 | 0.045 | 0.180 | 0.62 | 0.011 | 0.084 | 0.013 |
| 3-I-1 | 19.99 | 0.822 | 0.150 | 0.010 | 0.015 | 0.175 | 0.20 | 0.018 | 0.028 | 0.012 |
| 3-I-2 | 19.99 | 0.984 | 0.770 | 0.013 | 0.025 | 0.808 | 0.25 | 0.019 | 0.018 | 0.014 |
| 3-I-3 | 20.00 | 0.957 | 0.200 | 0.021 | 0.048 | 0.269 | 0.36 | 0.028 | 0.024 | 0.013 |
| 3-I-4 | 20.02 | 0.661 | 0.330 | 0.015 | 0.039 | 0.384 | 0.41 | 0.013 | 0.037 | 0.011 |
| 4-I-1 | 20.01 | 0.763 | 3.000 | 0.009 | 0.017 | 3.026 | 0.13 | 0.120 | 0.019 | 0.013 |
| 4-I-2 | 19.99 | 0.801 | 0.880 | 0.016 | 0.064 | 0.960 | 0.73 | 0.750 | 0.038 | 0.026 |
| 4-I-3 | 20.02 | 0.738 | 3.820 | 0.015 | 0.037 | 3.872 | 0.47 | 0.044 | 0.032 | 0.061 |
| 5-I-1 | 19.98 | 0.561 | 0.390 | 0.009 | 0.034 | 0.433 | 0.38 | 0.025 | 0.040 | 0.007 |
| 5-I-2 | 19.99 | 0.701 | 0.140 | 0.016 | 0.043 | 0.199 | 0.43 | 0.010 | 0.009 | 0.005 |
| 2-J-1 | 20.09 | 0.763 | 0.230 | 0.013 | 0.053 | 0.296 | 0.75 | 0.030 | 0.093 | 0.018 |
| 2-J-2 | 20.02 | 1.601 | 0.240 | 0.041 | 0.087 | 0.368 | 0.81 | 0.097 | 0.046 | 0.025 |
| 2-J-3 | 20.00 | 1.097 | 1.750 | 0.033 | 0.044 | 1.827 | 0.56 | 0.110 | 0.044 | 0.015 |
| 2-J-4 | 20.00 | 1.989 | 0.260 | 0.035 | 0.078 | 0.373 | 0.65 | 0.016 | 0.025 | 0.013 |
| 3-J-1 | 20.00 | 0.867 | 0.320 | 0.033 | 0.120 | 0.473 | 1.18 | 0.160 | 0.018 | 0.009 |
| 3-J-2 | 20.06 | 0.834 | 0.940 | 0.014 | 0.077 | 1.031 | 0.79 | 0.022 | 0.055 | 0.011 |
| 3-J-3 | 20.02 | 0.676 | 0.520 | 0.067 | 0.037 | 0.624 | 0.31 | 0.033 | 0.160 | 0.019 |
| 1-K-1 | 20.00 | 1.095 | 0.110 | 0.031 | 0.053 | 0.194 | 0.75 | 0.013 | 0.010 | 0.011 |
| 1-K-2 | 20.01 | 1.202 | 0.320 | 0.032 | 0.060 | 0.412 | 0.69 | 0.014 | 0.022 | 0.016 |
| 2-K-1 | 20.04 | 0.920 | 0.450 | 0.028 | 0.028 | 0.506 | 0.33 | 0.017 | 0.021 | 0.017 |
| 2-K-2 | 19.99 | 0.654 | 0.290 | 0.009 | 0.016 | 0.315 | 0.25 | 0.013 | 0.024 | 0.012 |

[1] 2 birds.
[2] 7 birds.
[3] 8 birds.
[4] 14 birds.

*Acknowledgment*

Collections were made by field personnel of the Bureau of Sport Fisheries and Wildlife. Regional Pesticide Specialists of the Division of Wildlife Services were responsible for coordinating and reporting collections and assuring that samples were received by the contracting laboratory in proper condition. The Regional Pesticide Specialists are:

| | |
|---|---|
| James B. Elder | Twin Cities, Minn. |
| Robert H. Hillen | Albuquerque, N. Mex. |
| David J. Lenhart | Portland, Oreg. |
| John C. Oberheu | Atlanta, Ga. |
| John W. Peterson | Boston, Mass. |


See Appendix for chemical names of compounds discussed in this paper.

## LITERATURE CITED

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# *The Occurrence of Mirex in Starlings Collected in Seven Southeastern States—1970* [1]

John C. Oberheu

ABSTRACT

*Selected samples of starlings collected for the National Pesticides Monitoring Program were analyzed for mirex, the chemical used for eradication of the imported fire ant. Whole bodies (less skin, beak, feet, and outer wings) of 10 birds from each sampling site were pooled for analysis. Residues present in 10 of the 12 sample pools ranged from 0.01 to 1.66 ppm.*

## *Introduction*

During the fall of 1970, the U. S. Department of Agriculture planned to treat 120 million acres in the southeastern United States with mirex to eradicate the imported fire ant. Very little information was available on the uptake of mirex in animal food chains, and there was widespread concern among conservationists about the environmental hazards of this chemical.

During November and December 1970, samples of starlings (*Sturnus vulgaris*) were collected by the Bureau of Sport Fisheries and Wildlife from designated sampling sites throughout the country as a part of the national pesticides monitoring network, described by Dustman *et al.* (*2*). Since the standard analysis of these monitoring samples does not include determination of mirex residues, arrangements were made for special analysis of samples collected in seven of the States which either had been or would be treated in the fire ant eradication program. This paper presents the results of these analyses. Data on organochlorine residues in the nationwide starling monitoring samples are reported separately by Martin and Nickerson (*5*); mercury and lead data are included in Martin (*4*).

## *Sampling and Analytical Procedures*

Details on selection of sample sites, methods of collection, and analytical procedures for the starling samples were described by Martin (*3,4*) and Martin and Nickerson (*5*). Each sample consisted of a pool of 10 starlings collected by trapping or shooting. Specimens were wrapped in aluminum foil, placed in plastic bags, and frozen immediately. They were kept frozen until processed for analysis by the Wisconsin Alumni Research Foundation.[2]

The birds were skinned, and beaks, legs, and outer wings were clipped off. The bodies were ground thoroughly in a Hobart food chopper. A 20-g portion of the homogenate was weighed into a 150-ml beaker and placed in a 40° C oven for 72-96 hours. After dry-weight calculation, the samples were ground with 100 g of $Na_2SO_4$ and placed in a 33-x 94-mm Whatman extraction thimble. Samples were extracted for 8 hours on a Soxhlet extractor using 70 ml of ethyl ether and 170 ml of petroleum ether. The solvent was concentrated to 10-15 ml on a steam bath and made to 50 ml with petroleum ether.

Cleanup was accomplished by placing an aliquot of the sample on previously standardized Florisil (*1*). Typical elutions were 150 ml of 5% ethyl ether in petroleum ether, followed by 240 ml of 15% ethyl ether in petroleum ether. The resulting solutions were concentrated on a steam bath (10-15 ml) and made to 25 ml with hexane.

[1] From the Bureau of Sport Fisheries and Wildlife, U. S. Department of the Interior, Atlanta, Ga. 30323.

[2] Mention of this commercial laboratory is for identification only and does not constitute endorsement by the U. S. Department of the Interior.

A 10-$\mu$l portion of the sample solution was injected into a Barber-Coleman, Model 5360, gas chromatograph, operating with the following instrument conditions:

| | | |
|---|---|---|
| Column: | Glass, 4′ x 4 mm, packed with 5% DC-200 on 80/100 Gas Chrom Q | |
| Temperatures: | Column | 210° C |
| | Injector | 230° C |
| | Detector | 240° C |
| Carrier gas: | Nitrogen | |
| Flow rate: | Mirex off column in 12-15 minutes | |

### *Results*

Table 1 presents the residue levels of mirex in starlings from the 12 collection sites, a history of the nearest mirex treatments, and each site's rated potential for accumulating residues.

All but two of the samples contained detectable levels of mirex. The highest levels occurred at Anniston, Ala., and Thomaston, Ga., both locations of high exposure potential. Although starlings are known to be migratory birds that can range widely for food, the residues occurring in most of the samples correspond generally with the exposure potential. The significance of these residue levels in birds is not presently known. The occurrence in 10 out of 12 samples does, however, prove that mirex will readily appear in animal food chains despite the very low dosage (1.7 g per acre) at which it is applied (*6*).

See Appendix for chemical name of mirex.

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TABLE 1.—*Levels of mirex in starlings, history of mirex treatment, and exposure potential for 1970 collection sites*

| Sample Site Location | Mirex Residues (ppm) [1] | Nearest Mirex Treatment | Dates of Treatment | Exposure Potential |
|---|---|---|---|---|
| Penderlee, N. C. | ND | 65 miles | Spring and fall of 1966, 1968, and 1969 | Low |
| Monroe, N. C. | ND | 100 miles | Spring and summer 1963, summer 1964, spring 1965 and fall 1967 | Low |
| Aiken, S. C. | 0.08 | Treated (5,000 acres) | Fall of 1966 and 1967, spring 1970 | Moderate to high |
| Carthage, Miss. | 0.08 | 15 miles (855,000 acres) | Spring 1967 | Low to moderate |
| Gulfport, Miss. | 0.42 | Treated (75,000 acres) | Summer 1969 | Moderate to high |
| Alexandria, La. | 0.10 | Treated (802,000 acres) | Spring and fall 1965, spring 1966 | Low |
| Anniston, Ala. | 1.61 | Immediately adjacent (5,000 acres) | Spring 1970. Bait available for landowner treatments | High |
| Thomaston, Ga. | 1.66 | 3 miles (1,840,000 acres) | Fall 1969 | Moderate to high |
| Jessup, Ga. | 0.62 | Treated (200,000 acres) | Spring and fall 1970 | High |
| Panama City, Fla. | 0.31 | Same county (800 - 2,240 acres) | Fall 1964 and 1965, spring 1966 and 1967 | Low to moderate |
| Madison, Fla. | 0.01 | 75 miles (1,000 acres) | Annual treatment since 1965 | Low |
| Winter Haven, Fla. | 0.34 | Treated (368,000 acres) | Spring and summer 1967. County treatments of 2,500-368,000 acres annually 1964-69 | Moderate |

NOTE: ND = not detected.
[1] Wet-weight basis.

# *Organochlorine Pesticide Residues in Commercially Caught Fish in Canada—1970*

J. Reinke,[1] J. F. Uthe,[1] and D. Jamieson [2]


## ABSTRACT

*Organochlorine pesticide residues were determined for commercially caught fish from a total of 78 locations in 68 central Canadian lakes and rivers. Only a few of these waters yielded fish with appreciable concentrations of DDT and its analogs (>1 ppm), and in only a few cases did the concentrations exceed the maximum permissible level of 5 ppm. Of the other organochlorine pesticides commonly used, namely lindane, aldrin, heptachlor, heptachlor epoxide, endrin, dieldrin, and chlordane, only dieldrin was found at significant levels in a number of samples, but these amounts were still below the maximum permissible level. Trace amounts of lindane were found in some samples. The presence of polychlorinated biphenyls (PCB's) was noted in samples from the Great Lakes and the south end of Lake Winnipeg. All results were confirmed by multiple-column gas chromatography and thin layer chromatography. PCB's were separated from DDE on aluminum oxide G (type E) plates run in a triethylamine-hexane solvent system.*


## *Introduction*

In recent years the fishing industry as a whole has suffered adversely from the effects of a wide variety of pollutants. The finding of extremely high concentrations of DDT in coho salmon (*Oncorhynchus kisutch*) from the Great Lakes (*6*) and northern anchovy (*Engraulis mordax*) off Los Angeles (*7*) has led to certain species being banned from the market and, undoubtedly, has resulted in public distrust of some fish products. Similiarly, the recent fishery disasters due to mercury, although eliminating contaminated products from the market, have caused adverse publicity resulting in reduced sales (*3*). To meet the need created by these incidents for a detailed survey of organochlorine pesticide residues in fish from commercially fished lakes and rivers in central Canada, a study was carried out in 1970 on fish collected from 78 locations in 68 Canadian waters (Fig. 1) and is reported here.

All analyses were done in duplicate, with all pesticides being determined by quantitation of gas-liquid chromatograms obtained from two different column packings; the second column packing was chosen to separate pesticides not widely separated by the first column. The identities of the pesticides were confirmed by thin layer chromatography.

## *Materials and Methods*

### SAMPLING PROCEDURES

Fish samples were collected from commercial fishermen by officers of the Inspection Service of the Department of Fisheries and Forestry. A sample consisted of 5 lb of headless dressed fish; if the fish were large, as few as three were pooled to make up a sample. The fish were frozen and shipped to Winnipeg where they were ground (Hobart, Model L800); a 2-lb portion of each sample was refrozen in a block and stored at −40° C until analyzed.

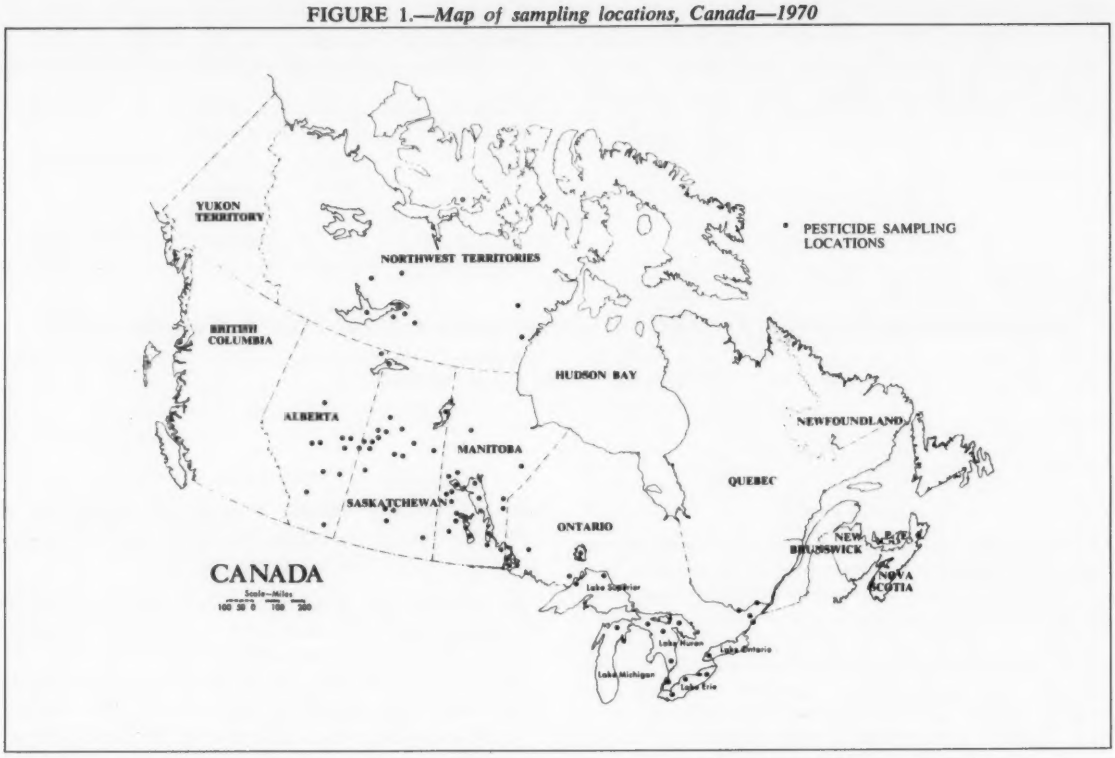
### ANALYTICAL PROCEDURES

For sample extraction, the method of Mills *et al.* (*4*) was used with slight modifications. Hexane, petroleum ether, and acetonitrile were purchased as reagents certified for pesticide analysis. Acetone was redistilled prior to use, and diethyl ether was purified according to the method of Grussendorf *et al.* (*2*). A 25-g portion of fish was taken from the center of the frozen sample block and blended with 75 ml of acetonitrile for 2 minutes at high speed in a Waring blender (Model B). The homogenate was suction filtered through a sintered glass funnel directly into a 1-liter separatory funnel and re-extracted twice with 25 ml of acetonitrile; then, 350 ml of distilled water, 7 ml of saturated aqueous NaCl.

[1] Fisheries Research Board of Canada, Freshwater Institute, Winnipeg 19, Manitoba.

[2] Department of Fisheries, Inspection Branch, Winnipeg, Manitoba.

FIGURE 1.—*Map of sampling locations, Canada—1970*




and 57 ml of petroleum ether were added to the separatory funnel, shaken vigorously, and allowed to separate into layers. The aqueous layer was discarded, and the organic layer was washed twice with 100 ml of water and drained into a 100-ml graduated cylinder; the recovered petroleum ether was then measured to determine the correction factor, transferred to a 250-ml round bottom flask, and reduced to approximately 1 ml on a rotary evaporator at 40° C.

The sample was quantitatively transferred to the cleanup column by rinsing the round bottom flask with two 10-ml aliquots of 8% ether-hexane. The column was made up of 30 g of 2% $H_2O$-deactivated Florisil (60/80 mesh, PR grade, Floridin Co.) with ½ inch of anhydrous $Na_2SO_4$ (reagent grade, Fisher Scientific) above and below the Florisil. The Florisil had been stored at 130° C prior to deactivation; after deactivation, it had been slowly tumbled for ½ hour, then left to equilibrate further for 24 hours. It was then stored in a glass-stoppered bottle and was stable for 1 week.

The pesticides were eluted with 8% diethyl ether:hexane (8:92; v/v) to give a total eluate of 220 ml. This eluate was evaporated on a rotary evaporator to approximately 1 ml and then made up to the required volume with hexane prior to gas chromatography. All pesticides reported were confirmed by thin layer chromatography.

### *Gas-Liquid Chromatography*

A Hewett-Packard Model 5750, fitted with a pulsed d.c. $Ni^{63}$ electron capture detector, was used for gas chromatographic analysis. Operating parameters were as follows:

| | | |
|---|---|---|
| Columns: | Glass, 6′ x ¼″, o.d., packed with either 2% SE-30/3% QF-1 or 3% OV-225 on 80/100 mesh HMDS treated Chromosorb W. | |
| Temperatures: | Injection port | 230° C |
| | Column oven | 200° C |
| | Detector | 260° C |
| Carrier gas: | Helium | |
| Purge gas: | 10% methane in argon | |

Standard solutions (1 μg/ml) of lindane, aldrin, heptachlor, heptachlor epoxide, endrin, *p,p′*-DDE, *p,p′*-DDT, *p,p′*-DDD, *o,p′*-DDT, and dieldrin were prepared in hexane. Each standard gave a single peak on gas chromatography and a single spot on a thin layer plate. The chlordane standard was reported tc be 95% α-chlordane; gas chromatography showed two peaks only.

Quantitation was based on the peak heights obtained on injection of known amounts of pesticides. Care was taken to ensure that all heights were within the linear range of the detector, and, rather than make extrapolations, the samples were diluted. The following calcula-

tions were used to determine parts per million of residues in fish samples:

$$\text{ppm of residue} = \frac{\text{ng}/5\ \mu\text{l}}{x/n} \times \text{c.f.}$$

$x$ = weight of samples
$n$ = number of milliliters in final volume
5 $\mu$l = volume injected

$$\text{ng in volume injected} = \frac{\text{peak height of sample}}{\text{peak height of standard}}$$

$$\text{correction factor (c.f.)} = \frac{\text{ml petroleum ether recovered}}{\text{ml petroleum ether used}}$$

### *Thin Layer Chromatography*

Aluminum oxide G (E. Merck, Darmstadt) plates, 0.5 mm thick, were prepared according to the method of Moats (*5*). The plates were run in a hexane:triethylamine (Eastman Co.) solution (100:7, v/v).

Retention factors for pesticides confirmed by TLC are as follows:

| *Compounds* | *Retention Factors* |
|---|---|
| Methoxychlor | .119 |
| Lindane | .223 |
| *p,p'*-DDD | .224 |
| Dieldrin | .268 |
| Chlordane | |
| cis | .283 |
| trans | .328 |
| Heptachlor epoxide | .328 |
| BHC | .335 |
| Endrin | .358 |
| *p,p'*-DDT | .388 |
| *o,p'*-DDT | .447 |
| Heptachlor | .597 |
| *p,p'*-DDE | .611 |
| Aldrin | .642 |
| PCB's (five spots) | .436, .530, .536, .657, .751 |

This particular solvent system was chosen because it separated the pesticides and at the same time separated the PCB spots in a manner which allowed for DDE identification and isolation. This method is sensitive to 1.0 $\mu$g for visible identification. If spots were not visible, the area was scraped and eluted with 1:1 hexane:acetone and injected to the gas chromatograph for confirmation.

#### RECOVERY STUDIES

During the course of the survey, recovery studies were performed every other month. The studies were carried out by spiking previously analyzed samples with known amounts of the desired pesticides. The difference between the spiked and the unspiked result was used to indicate the percent recovered. Similar studies were performed with blanks at various steps in the analyses. Recovery values shown below represent the average values of all eight recovery studies carried out:

| | | | |
|---|---|---|---|
| Heptachlor | 72% | *p,p'*-DDT | 84% |
| Aldrin | 72% | *p,p'*-DDD | 90% |
| Heptachlor epoxide | 77% | *p,p'*-DDE | 90% |
| Lindane | 80% | *o,p'*-DDT | 94% |
| Endrin | 81% | Dieldrin | 100% |

The standard deviation for all pesticides was ±6%.

The results of recovery studies showed lower recovery values for the compounds with lower boiling points, i.e., lindane, heptachlor, aldrin, endrin, and heptachlor epoxide. Also, recovery values for these compounds were lower than results of Brown (*1*) in his comparison of the Mills and Langlois cleanup procedures using fatty and non-fatty samples. Brown's recovery results (*1*), however, are lower for the remaining pesticides examined except for DDD in fish oil in which he had a recovery of 111%; this was apparently due to both *o,p'*-DDT and *p,p'*-DDD peaks eluting simultaneously under his GLC conditions. Because small amounts of only a few pesticides with low boiling points were found, their lower recovery values, in this instance, are not considered to be critical.

The cause of the low recovery values for the compounds mentioned above could be the fact that the sample volume was reduced two times by rotary vacuum evaporator before it was ready for gas-chromatographic analyses.

Results were expressed without correction for percent recovery.

### *Results and Discussion*

Pesticides were found in fish from most of the 68 lakes and rivers sampled (Table 1). However, the only waters which showed significant amounts of DDT and its analogs (>1 ppm) were in the Provinces of Ontario and Alberta and are as follows:

| *Province of Ontario* | *Province of Alberta* |
|---|---|
| The Great Lakes | Lake St. Paul |
| Huron | Sturgeon River |
| Erie | Cold River |
| Ontario | Bow River |
| Michigan | |
| Superior | |
| Lake St. Clair | |
| Lake Nipigan | |
| Ottawa River | |

Of the pesticides analyzed for, DDT and its analogs appeared most often with dieldrin appearing almost as

frequently. PCB's were quite prominent throughout the Great Lakes and appeared to a lesser degree in southern Lake Winnipeg in Manitoba and in the Bow River area of Alberta. It should be noted that, because of the interference of PCB's with DDT and its analogs, the DDT results of the survey in the areas where PCB's were found may, to some extent, be erroneous, but thin layer studies indicated that the reported values would be higher by 10% at most. The fact that not all regions with DDT present in fish samples had PCB's present would indicate that PCB's are not being used to extend the kill life of organochlorine pesticides and that these compounds do not enter the environment as a breakdown product of pesticides. Trace amounts of other pesticides (especially lindane, heptachlor, and heptachlor epoxide) were found in the Great Lakes, some lakes in northern Manitoba and Saskatchewan, and in many lakes in the Northwest Territories.

Results showed that pesticide concentrations differed for various species in the same lake and that the pesticide concentrations in the same species varied with body size and weight.

See Appendix for chemical names of compounds discussed in this paper.

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TABLE 1.—*Pesticide residue levels in fish, by provinces and waters, Canada—1970*
[T = trace = <0.005 ppm; — = not detected]

| Lake or River [1] | Latitude and Longitude | Fish Species | Pesticide Residue Levels (PPM) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Dieldrin | *p,p'*-DDE | *o,p'*-DDT | *p,p'*-DDD | *p,p'*-DDT | Total DDT |
| **PROVINCE OF ONTARIO** | | | | | | | | |
| Lake Huron | 44° 30′ 82° 15′ | Coho salmon | — | 2.20 | 0.70 | 0.80 | 1.30 | 5.00 |
| | | do. | — | 8.90 | 1.20 | 1.50 | 3.90 | 15.50 |
| | | do. | — | 6.70 | 0.70 | 1.00 | 2.60 | 11.00 |
| (Manitoulin Is.) | | do. | 0.16 | 1.80 | 0.20 | 0.50 | 0.80 | 3.30 |
| (Georgian Bay) | | do. | 0.40 | 11.10 | 0.90 | 1.40 | 3.00 | 16.40 |
| Do. | | do. | 0.20 | 5.60 | 0.90 | 1.40 | 2.00 | 10.60 |
| Do. | | do. | 0.20 | 1.00 | 0.30 | 0.30 | 0.70 | 2.30 |
| (Southern) | | do. | 0.07 | 0.49 | 0.12 | 0.17 | 0.51 | 1.20 |
| Do. | | do. | 0.08 | 0.55 | 0.17 | 0.16 | 0.56 | 1.44 |
| Do. | | do. | 0.08 | 0.43 | 0.18 | 0.13 | 0.41 | 1.15 |
| | | Whitefish | 0.15 | 0.20 | 0.11 | 0.08 | 0.38 | 0.83 |
| | | do. | 0.15 | 0.23 | 0.12 | 0.07 | 0.33 | 0.75 |
| | | do. | 0.12 | 0.26 | 0.13 | 0.08 | 0.44 | 0.91 |
| (Northern) | | do. | 0.21 | 0.36 | 0.20 | 0.15 | 0.86 | 1.57 |
| Do. | | do. | 0.25 | 0.47 | 0.20 | 0.12 | 0.58 | 1.37 |
| (Northern) | | Kokanee | 0.20 | 0.50 | 0.10 | 0.10 | 0.60 | 1.30 |
| (Georgian Bay) | | Yellow pickerel | 0.01 | 0.19 | 0.04 | 0.55 | 0.18 | 0.47 |
| (Northern) | | do. | 0.15 | 1.68 | 0.28 | 0.46 | 1.87 | 4.29 |
| (Georgian Bay) | | Sturgeon | — | 0.32 | — | 0.12 | 0.18 | 0.62 |
| Do. | | Yellow perch | 0.03 | 0.43 | 0.14 | 0.14 | 0.75 | 1.46 |
| (Northern) | | Mullets | 0.14 | 0.90 | 0.26 | 0.38 | 1.45 | 2.99 |
| (Georgian Bay) | | Chub | 0.31 | 0.72 | 0.46 | 0.31 | 1.59 | 3.08 |
| | | Rainbow trout | 0.17 | 0.60 | 0.32 | 0.22 | 0.88 | 2.02 |
| Lake Erie | 42° 53′ 78° 56′ | Mullets | 0.04 | 0.18 | 0.01 | 0.18 | 0.13 | 0.50 |
| | | do. | 0.03 | 0.17 | 0.02 | 0.18 | 0.13 | 0.50 |
| (Western) | | Perch | 0.04 | 0.14 | 0.01 | 0.14 | 0.13 | 0.49 |
| Do. | | do. | 0.04 | 0.16 | 0.02 | 0.17 | 0.14 | 0.92 |
| | | Catfish | 0.11 | 0.49 | 0.13 | 0.73 | 0.33 | 1.68 |
| | | Carp | 0.08 | 0.51 | 0.02 | 0.37 | 0.06 | 0.96 |

TABLE 1.–*Pesticide residue levels in fish, by provinces and waters, Canada–1970*–Continued

| Lake or River [1] | Latitude and Longitude | Fish Species | Pesticide Residue Levels (PPM) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Dieldrin | *p,p'*-DDE | *o,p'*-DDT | *p,p'*-DDD | *p,p'*-DDT | Total DDT |
| **PROVINCE OF ONTARIO—Continued** | | | | | | | | |
| Lake Erie (Cont'd) | | Alewife | 0.56 | 0.17 | — | — | 0.18 | 0.34 |
| | | Sheepshead | 0.06 | 0.27 | 0.03 | 0.35 | 0.27 | 0.92 |
| Lake Ontario | 43° 45′ 78° 00′ | Pickerel | 0.06 | 0.71 | 0.20 | 0.35 | 0.37 | 1.63 |
| | | do. | 0.07 | 0.53 | 0.21 | 0.33 | 0.41 | 1.48 |
| | | do. | 0.08 | 0.55 | 0.19 | 0.33 | 0.40 | 1.47 |
| | | Rockbass | 0.01 | 0.07 | — | 0.04 | 0.02 | 0.13 |
| | | Lake herring | 0.28 | 2.64 | 0.58 | 0.43 | 2.84 | 6.49 |
| | | Crappies | 0.02 | 0.17 | 0.28 | 0.12 | 0.12 | 0.45 |
| | | Pike | — | — | — | — | — | — |
| | | Perch | 0.15 | 0.67 | — | 0.42 | 0.69 | 1.78 |
| | | Whitefish | 0.37 | 0.65 | — | 0.67 | 0.57 | 1.89 |
| Lake Michigan | 43° 45′ 87° 00′ | Alewife | 0.14 | 3.72 | 0.37 | 0.56 | 1.19 | 4.28 |
| | | Chub | 0.03 | 2.50 | 0.68 | 0.44 | 3.00 | 6.62 |
| Lake Superior | 48° 00′ 88° 00′ | Smelt | — | 0.16 | — | — | T | 0.16 |
| | | Lake trout | 0.06 | 0.68 | 0.11 | 0.16 | 0.36 | 1.32 |
| St. Clair | 47° 14′ 84° 00′ | Coho | 0.03 | 0.12 | 0.05 | 0.05 | 0.15 | 0.37 |
| | | Pickerel | 0.10 | 1.11 | 0.12 | 0.58 | 1.09 | 2.90 |
| Sturgeon River | 46° 19′ 79° 58′ | Mullet | 0.01 | 0.14 | 0.05 | 0.20 | 0.52 | 0.91 |
| Nipigon | 49° 50′ 88° 30′ | Northern pike | — | 0.23 | 0.04 | 0.04 | 0.14 | 0.45 |
| | | Pickerel | — | 0.20 | 0.04 | 0.03 | 0.09 | 0.36 |
| | | Whitefish | 0.05 | 0.80 | 0.15 | 0.05 | 0.47 | 1.47 |
| | | Tullibee | 0.06 | 0.80 | 0.28 | 0.43 | 0.92 | 2.45 |
| Lake of the Woods | 49° 00′ 94° 50′ | Whitefish | 0.01 | 0.12 | 0.01 | 0.05 | 0.02 | 0.20 |
| | | do. | 0.03 | 0.16 | 0.04 | 0.08 | 0.05 | 0.33 |
| Ottawa River | 45° 34′ 74° 23′ | Crappies | 0.01 | 0.11 | 0.02 | 0.02 | 0.05 | 0.20 |
| | | Bullheads | 0.03 | 0.08 | — | 0.95 | 0.67 | 0.24 |
| | | do. | 0.03 | 0.08 | — | 0.95 | 0.67 | 0.24 |
| | | Sturgeon | 0.52 | 0.82 | 0.51 | 0.89 | 1.14 | 3.36 |
| St. Lawrence | 45° 20′ 73° 58′ | Yellow perch | — | 0.01 | — | 0.80 | 0.01 | 0.23 |
| | | Bullheads | 0.03 | 0.88 | — | 0.24 | 0.05 | 0.38 |
| Lake St. Francis | 45° 08′ 74° 25′ | Yellow perch | 0.03 | 0.05 | — | 0.04 | 0.06 | 0.15 |
| Clay | 50° 05′ 93° 30′ | Pike | 0.01 | 0.02 | — | 0.02 | 0.07 | 0.17 |
| | | Whitefish | 0.07 | 0.02 | — | 0.02 | 0.06 | 0.10 |
| **PROVINCE OF MANITOBA** | | | | | | | | |
| Winnipegosis | 52° 30′ 100° 00′ | Goldeye | T | 0.01 | T | T | — | 0.01 |
| (Dawson Bay) | | do. | 0.01 | 0.02 | 0.02 | 0.01 | — | 0.05 |
| (N) | | Mullet | T | 0.01 | T | T | — | 0.01 |
| (S) | | do. | T | 0.01 | T | T | — | 0.01 |
| (Duck Bay) | | do. | T | T | T | T | T | T |
| (Dawson) | | do. | T | 0.01 | — | T | — | 0.01 |
| (N) | | Sauger | T | T | T | T | T | T |
| (Duck Bay) | | do. | T | 0.01 | T | T | T | 0.01 |
| (S) | | do. | T | T | — | — | T | T |
| (S) | | Northern pike | T | T | T | T | T | T |
| (N) | | do. | T | 0.01 | T | T | T | 0.01 |
| (Duck Bay) | | do. | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.04 |
| (N) | | Pickerel | T | T | T | T | T | T |
| (S) | | do. | T | 0.02 | T | T | T | 0.02 |
| (Duck) | | do. | T | 0.02 | T | T | T | 0.02 |
| (Dawson) | | do. | T | 0.01 | — | T | — | 0.01 |
| God's | 50° 40′ 94° 15′ | Pike | — | — | — | — | — | — |
| | | Walleye | — | — | — | — | — | — |
| Reindeer | 57° 20′ 102° 00′ | Lake trout | — | — | — | — | — | — |
| Family | 51° 54′ 95° 27′ | Walleye | — | T | — | — | — | T |
| | | Pike | — | T | — | — | — | T |
| Fishing | 52° 08′ 95° 24′ | Walleye | — | T | — | — | — | T |
| Winnipeg | 52° 00′ 97° 00′ | Pike | 0.01 | 0.15 | 0.01 | 0.09 | 0.05 | 0.30 |
| (Southern) | | Sauger | 0.02 | 0.11 | 0.03 | 0.09 | 0.02 | 0.25 |
| (Northern) | | Northern pike | 0.01 | 0.05 | 0.01 | 0.01 | 0.02 | 0.09 |
| (Southern) | | do. | 0.01 | 0.19 | 0.02 | 0.12 | 0.08 | 0.41 |

TABLE 1.—*Pesticide residue levels in fish, by provinces and waters, Canada—1970*—Continued

| Lake or River [1] | Latitude and Longitude | Fish Species | Pesticide Residue Levels (PPM) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Dieldrin | *p,p'*-DDE | *o,p'*-DDT | *p,p'*-DDD | *p,p'*-DDT | Total DDT |
| **PROVINCE OF MANITOBA—Continued** | | | | | | | | |
| Winnipeg (Cont'd) | | | | | | | | |
| (Northern) | | Pickerel | 0.01 | 0.04 | 0.01 | 0.01 | 0.01 | 0.07 |
| (Southern) | | do. | 0.01 | 0.16 | 0.02 | 0.04 | 0.31 | 0.53 |
| (Northern) | | Whitefish | 0.05 | 0.06 | 0.01 | 0.02 | 0.02 | 0.11 |
| | | do. | 0.01 | 0.08 | 0.03 | 0.06 | 0.09 | 0.26 |
| (Southern) | | Perch | T | 0.18 | 0.01 | 0.10 | 0.04 | 0.33 |
| Do. | | Sheepshead | 0.02 | 0.18 | 0.03 | 0.07 | 0.06 | 0.34 |
| | | Tullibee | 0.03 | 0.12 | 0.07 | 0.11 | 0.07 | 0.37 |
| Manitoba | 51° 00′ 98° 45′ | Mullet | T | T | T | T | T | T |
| | | Sauger | T | 0.03 | — | 0.01 | T | 0.04 |
| | | do. | T | 0.03 | T | 0.01 | T | 0.04 |
| (Northern) | | Northern pike | T | 0.02 | T | 0.02 | T | 0.04 |
| (Western) | | do. | — | 0.02 | T | 0.01 | T | 0.03 |
| (Southern) | | Pickerel | — | 0.02 | 0.01 | — | — | 0.03 |
| (Western) | | do. | T | 0.03 | 0.01 | 0.01 | 0.01 | 0.06 |
| St. Martin | 51° 37′ 98° 29′ | Mullet | T | 0.02 | T | 0.01 | T | 0.03 |
| | | Northern pike | T | 0.02 | T | T | 0.01 | 0.03 |
| | | Pickerel | T | 0.02 | T | T | 0.01 | 0.03 |
| | | Perch | T | 0.02 | T | 0.01 | T | 0.03 |
| Dauphin | 51° 17′ 99° 48′ | Mullet | T | 0.02 | — | 0.01 | T | 0.03 |
| | | do. | T | 0.02 | — | 0.01 | — | 0.03 |
| | | Northern pike | T | 0.02 | — | 0.01 | — | 0.03 |
| | | do. | T | 0.01 | T | 0.01 | — | 0.02 |
| | | Pickerel | T | 0.02 | T | 0.01 | — | 0.03 |
| | | do. | T | 0.02 | 0.01 | 0.01 | T | 0.04 |
| Lockport | 50° 05′ 96° 56′ | Maria | T | 0.03 | T | 0.03 | 0.02 | 0.08 |
| South Indian | 57° 10′ 98° 30′ | Pickerel | T | 0.01 | T | T | T | 0.01 |
| Dogskin | 51° 43′ 95° 12′ | Pickerel | T | T | — | — | T | T |
| Cedar | 49° 55′ 96° 27′ | Northern pike | T | 0.05 | T | 0.02 | 0.03 | 0.10 |
| Clear | 50° 41′ 100° 00′ | Pickerel | — | 0.10 | — | 0.08 | 0.17 | 0.34 |
| Summerberry River | 53° 23′ 100° 22′ | Pike | T | T | — | — | — | T |
| **PROVINCE OF SASKATCHEWAN** | | | | | | | | |
| Dillon | 55° 45′ 109° 30′ | Northern pike | — | — | — | — | — | — |
| Buffalow Narrows | 55° 51′ 108° 29′ | Pickerel | T | T | T | — | T | T |
| Pelican | 50° 32′ 106° 00′ | Whitefish | T | 0.01 | 0.01 | 0.01 | — | 0.03 |
| Montreal | 54° 20′ 105° 40′ | Whitefish | 0.01 | 0.01 | 0.02 | 0.01 | — | 0.04 |
| Jackfish | 51° 39′ 101° 35′ | Whitefish | 0.01 | 0.02 | 0.03 | 0.01 | — | 0.06 |
| Last Mountain | 51° 05′ 105° 14′ | Whitefish | 0.01 | 0.01 | — | T | — | 0.01 |
| Primrose (Long Bay) | 54° 55′ 109° 45′ | Whitefish | 0.01 | 0.25 | 0.05 | 0.06 | 0.19 | 0.55 |
| | | do. | T | 0.05 | 0.01 | 0.04 | 0.05 | 0.15 |
| Pinehouse | 55° 32′ 106° 35′ | Whitefish | T | 0.01 | 0.01 | T | — | 0.02 |
| Weyakwin | 54° 30′ 106° 00′ | Whitefish | T | 0.01 | 0.01 | T | — | 0.02 |
| Lac La Ronge | 55° 04′ 105° 19′ | Whitefish | T | 0.01 | 0.01 | T | — | 0.02 |
| Ile La Cross | 55° 40′ 107° 45′ | Whitefish | — | 0.01 | 0.02 | — | — | 0.03 |
| Descharme | 57° 05′ 109° 13′ | Whitefish | 0.01 | T | — | 0.01 | — | 0.01 |
| Wicken Camp | 57° 29′ 109° 38′ | Whitefish | T | T | T | T | T | T |
| North Sask. River | 53° 15′ 105° 05′ | Burbot | T | 0.20 | — | 0.01 | 0.01 | 0.04 |
| | | do. | T | 0.10 | — | 0.01 | 0.01 | 0.03 |
| | | do. | T | 0.10 | — | 0.01 | 0.01 | 0.03 |
| | | do. | — | 0.02 | — | 0.19 | 0.19 | 0.40 |
| | | Goldeye | — | 0.22 | 0.29 | 0.22 | 0.22 | 0.95 |
| | | do. | 0.08 | 0.09 | 0.06 | 0.10 | 0.10 | 0.43 |
| Athabasca | 59° 15′ 109° 15′ | Pickerel | — | T | — | — | — | T |
| Utikumak | 54° 50′ 108° 14′ | Whitefish | — | 0.01 | 0.01 | — | — | 0.01 |

TABLE 1.–*Pesticide residue levels in fish, by provinces and waters, Canada–1970*–Continued

| Lake or River [1] | Latitude and Longitude | Fish Species | Pesticide Residue Levels (PPM) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Dieldrin | *p,p'*-DDE | *o,p'*-DDT | *p,p'*-DDD | *p,p'*-DDT | Total DDT |
| **PROVINCE OF ALBERTA** | | | | | | | | |
| Bellis | 54° 09′ 112° 09′ | Goldeye | 0.01 | 0.12 | 0.02 | 0.08 | 0.06 | 0.28 |
| | | do. | 0.02 | 0.23 | 0.02 | 0.15 | 0.12 | 0.52 |
| St. Paul | 59° 59′ 111° 17′ | Goldeye | 0.02 | 0.60 | — | 0.55 | 0.79 | 1.94 |
| | | Burbot | T | 0.04 | — | 0.02 | 0.03 | 0.09 |
| | | do. | T | 0.02 | — | 0.01 | 0.02 | 0.05 |
| | | do. | T | 0.02 | — | 0.02 | 0.02 | 0.06 |
| | | Walleye | T | 0.40 | 0.30 | 0.20 | 0.20 | 1.1 |
| | | Pike | — | 0.40 | 0.08 | 0.22 | 0.25 | 0.95 |
| | | Pickerel | 0.01 | 0.04 | — | 0.03 | 0.03 | 0.10 |
| Sturgeon River | 53° 46′ 113° 10′ | Whitefish | 0.03 | 0.08 | 0.08 | 0.08 | 0.23 | 0.47 |
| | | Goldeye | 0.06 | 0.37 | 0.48 | 0.28 | 1.08 | 2.21 |
| | | Pickerel | 0.01 | 0.04 | — | 0.03 | 0.05 | 0.12 |
| Kinnaird | 54° 47′ 111° 31′ | Northern Pike | T | T | 0.01 | — | — | 0.01 |
| Myrnam | 53° 40′ 111° 14′ | Pickerel | 0.01 | 0.06 | — | 0.04 | 0.05 | 0.15 |
| | | do. | 0.01 | 0.05 | — | 0.04 | 0.05 | 0.14 |
| Cold | 52° 18′ 112° 41′ | Tullibee | 0.01 | 0.34 | 0.02 | 0.02 | 0.10 | 0.48 |
| | | Whitefish | 0.02 | 0.89 | 0.08 | 0.09 | 0.70 | 1.76 |
| Lac La Biche | 54° 46′ 111° 58′ | Whitefish | — | 0.01 | 0.01 | — | — | 0.02 |
| Kackson | | Whitefish | 0.01 | T | — | 0.01 | — | 0.02 |
| Bow River | 49° 51′ 111° 41′ | Trout eggs | 0.92 | 0.57 | — | 0.39 | 0.37 | 1.33 |
| | | Rainbow trout | 0.05 | 0.50 | — | — | 0.32 | 0.87 |
| | | do. | 0.01 | 0.88 | 0.03 | 0.04 | 0.05 | 1.00 |
| | | do. | 0.05 | 0.35 | 0.29 | 0.26 | 0.43 | 1.33 |
| Whitemud Creek | 53° 27′ 113° 33′ | Northern sucker | 0.01 | 0.07 | 0.02 | 0.06 | 0.09 | 0.24 |
| **NORTHWEST TERRITORIES** | | | | | | | | |
| Great Slave | 61° 23′ 115° 38′ | Whitefish | 0.01 | 0.01 | T | T | T | 0.01 |
| Hjalmar | 61° 33′ 109° 25′ | Whitefish | 0.01 | 0.03 | — | — | — | 0.03 |
| | | Lake trout | T | 0.03 | — | — | — | 0.03 |
| Nonacho | 61° 42′ 109° 40′ | Whitefish | T | T | — | — | T | T |
| Rutledge | 61° 33′ 110° 47′ | Whitefish | 0.01 | 0.01 | 0.01 | T | T | 0.02 |
| | | Lake trout | T | 0.02 | — | — | — | 0.02 |
| | | do. | — | T | — | — | — | T |
| | | Muktuk | 0.07 | 0.16 | 0.05 | 0.10 | 0.10 | 0.41 |
| Merkley | 69° 45′ 107° 40′ | Whitefish | 0.01 | T | T | T | — | T |
| Gymer | | Whitefish | 0.01 | 0.01 | 0.01 | T | T | 0.02 |
| Gordon | 63° 10′ 113° 12′ | Trout | 0.01 | 0.05 | 0.03 | 0.01 | 0.02 | 0.11 |
| | | Whitefish | 0.03 | 0.10 | — | 0.04 | 0.05 | 0.19 |
| Mackay | 63° 55′ 110° 25′ | Whitefish | 0.02 | 0.08 | 0.03 | 0.02 | 0.03 | 0.16 |
| Cambridge Bay | 68° 03′ 105° 05′ | Arctic char | T | T | — | — | — | T |
| | | do. | — | — | — | — | — | — |
| | | Whale | — | — | — | — | — | — |
| Baker | 64° 00′ 96° 00′ | Whitefish | — | — | — | — | — | — |
| Kaminak | 62° 10′ 95° 00′ | Lake trout | — | — | — | — | — | — |
| Jackson | 62° 35′ 114° 18′ | Whitefish | T | — | — | 0.01 | — | 0.01 |

[1] Specific location within waters, if known, given in parentheses.

# *Residues of Organochlorine Pesticides,, Polychlorinated Biphenyls, and Mercury in Bald Eagle Eggs and Changes in Shell Thickness—1969 and 1970*

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ABSTRACT

*Twenty-three bald eagle eggs collected in Alaska, Maine, Michigan, Minnesota, and Florida during 1969 and 1970 were analyzed for organochlorine pesticides, polychlorinated biphenyls, and mercury. All eggs contained residues of DDE, dieldrin, PCB's, and mercury. Average residue concentrations were lowest in eggs from Alaska. Significant eggshell thinning has occurred among eggs from most major areas sampled. Some eggs contained DDE residues of the same magnitude as those that produced shell thinning in experimental species. High dieldrin residues in some eggs could be having an adverse effect on reproductive success.*

## *Introduction*

Bald eagle (*Haliaeetus leucocephalus*) populations and the reproductive success of this species have declined in many areas of the United States within the last 20 years (*1,3,32*). Several authors have related the decline of eagles and of other species of raptorial and fish-eating birds at the top of food chains to the adverse effects of organochlorine pesticides that are widespread in the environment (*6,7,11,26,27*). A reduction in eggshell thickness since the introduction and widespread use of organochlorine pesticides has been shown for a number of bird species (*7,26,27*); the adverse effects of DDT and dieldrin in combination and of DDE on reproductive success of a raptorial species have been shown experimentally (*23,35*). Previous studies of field-collected bald eagles and their eggs have reported organochlorine or heavy metal residues (*9,22,28,33*), causes of mortality (*4,22*), and mortality due to pesticide poisoning (*4,22,29,33*).

This paper reports the results of analyses for organochlorine pesticides, polychlorinated biphenyls (PCB's), and mercury residues in bald eagle eggs collected in Alaska, Maine, Michigan, Minnesota, and Florida during 1969 and 1970. Eggshell characteristics and reproductive success are discussed in relation to these residues.

## *Sampling Procedures*

One egg was collected from each of 15 nests during the normal incubation period; 11 of the nests were located in Alaska, 3 in Maine, and 1 in Michigan. Eight additional eggs collected after the normal incubation period included five eggs from four nests in Minnesota, two eggs from nests on the west coast of Florida, and one egg from a nest on Kodiak Island, Alaska.

Following collection in the field, each egg was usually wrapped in aluminum foil, individually packed in a container, and shipped to the Patuxent Wildlife Research Center. The length and breadth of each egg was measured in millimeters, and the volume of some eggs was measured by water displacement. The eggs were opened, and the age of embryos was estimated based on a 35-day incubation period. Egg contents were frozen prior to chemical analysis. Shells were air dried, and shell thickness was measured as previously described (*9*).

## *Chemical Analysis*

Eggs were analyzed individually for residues of organochlorine pesticides, polychlorinated biphenyls (PCB's), and mercury. Each egg was mixed in an Omnimixer; a

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20-g aliquot was removed for pesticide and PCB analysis; and a 5-g aliquot was removed for mercury analysis. The 20-g aliquots were ground with anhydrous sodium sulfate and extracted for 7 hours with hexane in a Soxhlet apparatus. Extracts were cleaned up and then divided into halves; one half was used for pesticide analysis and the other saved for PCB analysis.

For pesticide analysis, each cleaned extract was spotted on a thin layer plate, developed, and removed in four fractions as described by Mulhern *et al.* (*22*). All four fractions were analyzed separately by electron capture gas chromatography on a 3.8% UCW-98 on 80/100 Diatoport S column, and DDT residues in Fractions III or IV were confirmed on a 3% XE-60 column. The operating parameters for the UCW-98 and XE-60 columns are given in Table 1. Average recovery by this method was 85-96% with a detection limit of approximately 0.05 ppm. Residues were not corrected for recovery. In addition to zonal separation by thin layer chromatography (TLC) and analysis on two columns, residues in 20% of the samples were confirmed by TLC ($AgNO_3$ incorporated $Al_2O_3$ plate—5% benzene in hexane solvent).

TABLE 1.—*Chromatographic operating conditions using electron capture detection for pesticide analysis*

| | Columns, Glass ¼" O.D. | |
|---|---|---|
| | A | B |
| Column length | 4 feet | 6 feet |
| Liquid phase | 3.8% UCW-98 | 3% XE-60 |
| Support | Diatoport S | Gas Chrom Q |
| Mesh size | 80/100 | 60/80 |
| Column flow rate | 60 ml/min | 100 ml/min |
| Purge | 40 ml/min | — |
| Gas | 5% methane/argon | nitrogen |
| Temperature | 200° C | 170° C |
| Retention time of dieldrin | 8.6 minutes | 16.3 minutes |

PCB analysis was by TLC as described by Mulhern *et al.* (*21*).

Mercury analyses were for total mercury by a method developed by R.S. Christensen (*personal communication*). The procedure involves acid digestion of the tissue and extraction of the mercury from the liquid digest with dithizone (*20*). Mercury determination was made on the dithizone extract by flame atomic absorption spectrophotometry using the "sampling boat" technique (*8*). The average recovery from tissue samples fortified with both inorganic and organic mercury compounds was 91%. The limit of detection was 0.05 ppm.

The residue concentrations were calculated as micrograms per milliliter on the basis of total egg volume. This is converted to a ppm basis assuming a specific gravity of 1.0 as described by Stickel *et al.* (*33*). Measurements of length and breadth were used to estimate the volume of those eggs whose volumes were not determined by water displacement. The equation for this estimate was volume (ml) = 3.73 X length (cm) X breadth (cm) − 35.3 (L. F. Stickel, S. N. Wiemeyer, and L. J. Blus, *manuscript in preparation*).

### *Collection Dates and Embryonic Development of Samples*

Six eggs were collected from Kodiak Island between May 8 and 26, 1969; two were fresh with no signs of embryonic development while four contained 7- to 23-day-old embryos. An additional egg from Kodiak Island (Karluk Weir), collected on July 21, 1969, after it failed to hatch during the normal incubation period, was decomposed with no evidence of embryonic development; a small partion of this egg's contents may have been lost before it was opened.

Five eggs from the Admiralty Island area, Alaska, collected between May 13 and 15, 1970, contained embryos estimated to be more than 15 days old. One (Tiedman Island) was decomposed and had lost a small portion of its contents before it was opened.

Three eggs from nests in Maine were collected on April 14 and 15, 1969. One (Dyer Neck) was decomposed with no signs of embryonic development; however, the other two contained embryos 15 to 32 days old.

The single egg from Baraga County, Michigan, collected on April 14, 1969, appeared fresh and exhibited no visible signs of embryonic development.

Two eggs from Minnesota (Star Island, Rabideau Lake), collected on June 4 and 6, 1969, contained embryos 8 to 20 days old. Two additional eggs were collected from one nest in Minnesota (Six Mile Lake) on May 14, 1970; one contained a decomposed embryo 5 to 10 days old, and the addled contents of the other contained no evidence of embryonic development. An additional egg from Minnesota, collected on June 5, 1970, exhibited no indication of embryonic development in its addled contents.

Two eggs collected in Lee County, Florida, on March 7 and May 2, 1969, were badly dehydrated and contained no signs of embryonic development.

### *Results*

Results of the analyses for organochlorine pesticides, PCB's, and mercury are shown in Table 2. Average residue concentrations of organochlorines in bald eagle eggs from Alaska were the lowest found for any area in the United States to date. DDE residues in the eggs from the Admiralty Island area, excluding the one egg from South Midway Island, averaged only 0.95 ppm.

TABLE 2.—*Organochlorine pesticides, polychlorinated biphenyls, and mercury in bald eagle eggs collected in Alaska, Maine, Michigan, Minnesota, and Florida in 1969 and 1970*

[ND = not detected; T = <0.05 ppm]

| Nest Location | Shell Thickness (mm)[1] | Egg Volume (ml)[2] | Residue Concentration in ppm | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | *p,p'*-DDE | *p,p'*-DDD | *p,p'*-DDT | Dieldrin | Heptachlor Epoxide | PCB's | Mercury |
| **ALASKA—KODIAK 1969** | | | | | | | | | |
| Island Point | 0.51 | [134] | 1.60 | 0.07 | ND | 0.09 | 0.02 | 1.9 | 0.2 |
| Bird Island | 0.52 | [136] | 4.93 | 0.23 | ND | 0.30 | 0.06 | 5.4 | 0.2 |
| Spiridon Bay | 0.52 | [144] | 1.43 | 0.07 | ND | 0.06 | 0.01 | 1.7 | 0.2 |
| Grassey Point | 0.53 | [129] | 1.89 | 0.21 | ND | 0.12 | 0.02 | 1.8 | 0.1 |
| Uganik Island | 0.60 | [128] | 1.28 | 0.06 | ND | 0.06 | 0.02 | 1.7 | 0.3 |
| Fraser Lake | 0.58 | [126] | 1.16 | 0.05 | ND | 0.02 | 0.01 | 1.6 | 0.1 |
| Karluk Weir | 0.59 | [123] | 1.15 | 0.14 | ND | 0.05 | 0.01 | 1.4 | 0.1 |
| Average | 0.55 | | 1.92 | 0.12 | ND | 0.10 | 0.02 | 2.2 | 0.2 |
| **ALASKA, ADMIRALTY ISLAND AREA—1970** | | | | | | | | | |
| Tiedman Island | [0.60] | 102 | 0.83 | T | ND | T | ND | 0.85 | 0.1 |
| Fools Inlet | 0.60 | 103 | 1.81 | T | ND | T | ND | 0.84 | 0.3 |
| South Midway Island | [0.55] | 125 | 10.75 | T | ND | 0.22 | ND | 2.3 | 0.2 |
| Windfall Harbor | 0.68 | 151 | 0.25 | T | ND | 0.02 | ND | 0.43 | 0.2 |
| Swan Island | 0.60 | 133 | 0.91 | T | ND | 0.03 | T | 0.88 | 0.2 |
| Average[3] | 0.61 | | 2.91 | T | ND | 0.06 | T | 1.1 | 0.2 |
| **MAINE—1969** | | | | | | | | | |
| Franklin | 0.49 | 142 | 11.86 | 0.55 | 0.24 | 0.22 | 0.02 | 4.9 | 0.3 |
| Dyer Neck | [0.47] | 129 | 20.55 | 0.84 | 0.49 | 0.29 | 0.03 | 15.2 | 0.3 |
| Boyden Pond | 0.59 | 131 | 12.44 | 0.35 | 0.25 | 0.15 | 0.02 | 9.7 | 0.4 |
| Average | 0.52 | | 14.95 | 0.58 | 0.33 | 0.22 | 0.02 | 9.9 | 0.3 |
| **MICHIGAN—1969** | | | | | | | | | |
| Van Zellen's Camp | 0.51 | 112 | 39.46 | 1.12 | ND | 1.02 | 0.07 | 27.7 | 0.4 |
| **MINNESOTA—1969 AND 1970[4]** | | | | | | | | | |
| Star Island | 0.48 | [130] | 21.62 | 2.42 | ND | 2.29 | 0.17 | 12.4 | 0.3 |
| Rabideau Lake | 0.61 | [120] | 3.68 | 0.91 | ND | 0.63 | 0.11 | 8.0 | 0.3 |
| Cass Lake | 0.55 | 123 | 8.15 | 0.48 | ND | 0.62 | T | 6.2 | 0.3 |
| Six Mile Lake (1) | 0.53 | [124] | 2.37 | 0.07 | ND | 0.16 | ND | 2.2 | 0.2 |
| (2) | 0.55 | [135] | 7.27 | 0.42 | ND | 0.65 | T | 5.8 | 0.3 |
| Average | 0.55 | | 9.57 | 1.02 | ND | 0.99 | 0.08 | 7.7 | 0.3 |
| **FLORIDA—1969** | | | | | | | | | |
| Lee County—1 | 0.61 | [104] | 18.21 | 1.13 | 0.19 | 0.68 | 0.02 | 13.3 | 0.3 |
| Lee County—3 | 0.52 | [98] | 18.52 | 2.49 | 0.29 | 1.54 | 0.07 | 11.1 | 0.7 |
| Average | 0.57 | | 18.37 | 1.81 | 0.24 | 1.11 | 0.05 | 12.2 | 0.5 |

[1] Shell thicknesses in brackets may not be totally accurate due to disruption and/or loss of the shell membranes. These data have been excluded from Table 3 and from *Discussion* in the text.
[2] Volumes in brackets computed as stated in text.
[3] Trace considered to equal 0.025 ppm when computing averages.
[4] Parentheses designate different eggs from the same nest. Average computed on a nest basis.

Residues of dieldrin averaged 0.06 ppm in all of the eggs from the Admiralty Island area, while DDD was present in only trace amounts. Residues in eggs from Kodiak Island were slightly higher, averaging 1.92 ppm DDE, 0.12 ppm DDD, and 0.10 ppm dieldrin.

Residues in eggs from Maine collected in 1969 averaged 0.22 ppm dieldrin, 14.95 ppm DDE, 0.58 DDD, and 0.33 ppm DDT. Residues in Maine eggs collected in 1967 and 1968 averaged somewhat higher and contained 1.63 ppm dieldrin, 21.01 ppm DDE, 0.98 ppm DDD, and 0.50 ppm DDT (*9*).

The concentration of organochlorine pesticides in the eggs from Chippewa National Forest, Minnesota, in 1969 and 1970 was generally similar to that found in eggs collected in Wisconsin in 1968 (*9*), with the exception of the egg from Star Island collected in Minnesota in 1969, which contained much higher residue concentrations. Excluding the Star Island egg, the residues in the eggs from Minnesota (on a nest basis) averaged 5.55 ppm DDE, 0.55 ppm DDD, and 0.55 ppm dieldrin. The single egg from the Michigan shore of Lake Superior contained an unusually high concentration of DDE and a moderate concentration of dieldrin.

TABLE 3.—*Bald eagle eggshell parameters for eggs collected in 1968 to 1970 and changes from pre-1946 norms*

| Area | Mean Eggshell Thickness [1] (mm) | Percent Change from Pre-1946 Norms [2] | Mean Shell Weight [1] (g) | Percent Change from Pre-1946 Norms [2] | Mean Thickness Index [1,3] | Percent Change from Pre-1946 Norms [2] |
|---|---|---|---|---|---|---|
| Alaska—Kodiak | 0.5500 (7) | —10.4** | 12.460 (6) | —[4] 11.4** | 2.770 (6) | —14.1** |
| Alaska—Admiralty | 0.6267 (3) | + 2.2 | 15.715 (2) | — | 3.345 (2) | — |
| Great Lake States | 0.5486 (14) | —10.2** | 11.617 (11) | —10.8* | 2.777 (11) | —12.1** |
| Florida | 0.5183 (6) | —11.3* | 9.650 (6) | —19.1** | 2.567 (6) | —[4] 17.2** |
| Maine | 0.5425 (4) | —11.0* | 12.830 (2) | — | 2.750 (2) | — |

NOTE: Sample size is given in parentheses.
All parameters for all eggs could not be used because of the presence of the following conditions: loss and/or disruption of shell membranes, loss of portion of shell, residue of egg contents adhering to shell surfaces.
The current samples of eggs may not be entirely random.

[1] Means are calculated on a nest basis; data are, in part, from Krantz *et al. (9)*.
[2] Pre-1946 data from D. W. Anderson and J. J. Hickey *(unpublished)*.
[3] Ten times shell weight (g) divided by the product of the length and breadth (cm) as devised by Ratcliffe *(26)*.
[4] Sample variances unequal; method of determining significance level from Snedecor and Cochran *(31)*.
* Significant change from pre-1946 norm $P < 0.01$; T-test.
** Significant change from pre-1946 norm $P < 0.001$; T-test.

DDE in the eggs from Lee County, Florida, averaged 18.37 ppm, which was considerably higher than the 10.72 ppm average in the eggs from Everglades National Park in 1968 (*9*). Dieldrin residues in eggs from Lee County were 0.68 and 1.54 ppm, about two and six times the highest level found in the Everglades eggs, which ranged from 0.11 to 0.28 ppm (*9*).

Residues of PCB's were lower than residues of DDT plus its metabolites for most eggs in all areas except for the majority of eggs taken from Kodiak, Alaska. The highest concentration of PCB's occurred in the egg from Michigan. Average PCB concentrations in descending order were: Florida 12.2 ppm, Maine 9.9 ppm, Minnesota 7.7 ppm, Kodiak, Alaska 2.2 ppm, and Admiralty, Alaska 1.1 ppm.

Mercury concentrations were uniformly low in the eggs sampled and averaged 0.2-0.3 ppm, with the exception that a higher concentration (0.7 ppm) occurred in one of the two eggs from Florida. Borg *et al.* (*2*) found reduced hatchability of pheasant (*Phasianus colchicus*) eggs that contained 1.3 to 2.0 ppm mercury.

Eggshell thickness and weight of bald eagle eggs collected from 1968 to 1970 are compared in Table 3 with measurements of shells of eggs collected prior to the widespread use of organochlorine pesticides (D. W. Anderson and J. J. Hickey, *unpublished data*). Thickness and weight were found to decline significantly ($p<0.01$) in all areas where sufficient data were available, except for a nonsignificant ($p>0.05$) change in eggshell thickness for eggs from the Admiralty Island area. Hickey and Anderson (*7*) reported declines in shell weight of 18.0 and 19.8% for bald eagle eggs collected from two Florida counties since organochlorine pesticides were initially used.

Shells of eggs from individual nests in the recent sample from Kodiak, Alaska, were from 2 to 17% thinner than the pre-1946 norm. Shells from Admiralty, Alaska, were 2% thinner to 11% thicker than the earlier norm. The shells of some eggs from the Lake States were equal in thickness to the pre-1946 norm, and others varied from that to as much as 21% thinner than the earlier norm. Eggshells from Florida were 25% thinner to 4% thicker than the pre-1946 norm, and those from Maine were 3 to 20% thinner than the earlier norm. Only those eggs that could be measured accurately (those used in Table 3) were included in the above data.

## *Discussion*

Data on reproduction of bald eagles in the areas in which eggs were collected are included in Table 4.

Lockie, Ratcliffe, and Balharry (*11*), in a study of golden eagles (*Aquila chrysaetos*) in west Scotland, found that the proportion of eagles successfully rearing young doubled (from 31% to 69%) following the ban of dieldrin use in sheep dips, the average dieldrin residues in eagle eggs dropped significantly (from 0.87 ppm to 0.38 ppm) during the same period. The low residues of DDE and other organochlorine pesticides, other than dieldrin, in the eggs of the Scottish eagles are not believed to have been a significant factor in reproductive success. Lockie and Ratcliffe (*10*) earlier correlated reproductive failure with amounts of dieldrin exceeding 1.0 ppm in the eggs of these golden eagles. Potts (*25*) found a significant correlation between the residues of dieldrin in the eggs of shag (*Phalacrocorax aristotelis*) and reproductive failure; there was a sizeable increase in the percentage of clutches with no chicks surviving to the 10th day when there was more than 2.0 ppm dieldrin in the egg.

TABLE 4.—*Reference data on reproduction of bald eagles in the areas in which eggs were collected*

| Location | Year | Average Number of Young per Active Nest/Year | Percent of Active Nests in Which Young Were Raised | Reference |
|---|---|---|---|---|
| Karluk Lake, Kodiak National Wildlife Refuge, Alaska | 1959, 1961, 1962 | 1 | — | Hensel and Troyer *(5)* |
| Kodiak National Wildlife Refuge, Alaska | 1963 | 1.1 | 66 | Troyer and Hensel *(34)* |
| Admiralty Island, Alaska | 1966 | 1.4 | 88 | Robards and King *(30)* |
| Chippewa National Forest, Minnesota | 1963-70 | 0.8 | 52 | Mathisen *(12-18)* Mathisen and Stewart *(19)* |
| Maine | 1965 | — | 18 | Sprunt and Ligas *(32)* |
| Florida (west coast) | 1965 | — | 45 | Sprunt and Ligas *(32)* |
| Michigan (shores of Great Lakes) | 1967 | — | 6 | Postupalsky *(24)* |

One-half of the bald eagle eggs from Maine that have been analyzed, as well as single eggs from Michigan, Minnesota, Wisconsin, and Florida have contained more than 1.0 ppm dieldrin—see also Krantz *et al.* (*9*). If the results of Lockie *et al.* (*11*), regarding the adverse effects of dieldrin on golden eagle reproduction, are also applicable to reproductive success in bald eagles, then dieldrin could be a factor in bald eagle reproductive success in these areas.

The DDE residues in a few of the eggs reported here, as well as in a number of eggs reported previously (*9*), especially many of those from Maine, were similar in magnitude to those that have produced shell thinning in experimental sparrow hawks (*Falco sparverius*) fed a low dietary level of DDE (*35*).

Average declines in shell thickness, as expressed by shell weight or thickness index, greater than 17% have been accompanied by severe declines in populations and/or reproductive success in several species of raptorial birds (*7,26,27*); declines in shell thickness are commonly associated with an increased frequency of egg breakage (*7,23,26,27*). The decline in shell weight and thickness index of bald eagle eggs from Florida equalling that of some declining raptor populations, the presence of eagle eggshell fragments in two Kodiak, Alaska, nests at the time of the egg collection, and the moderate declines in shell thickness for most of the areas sampled induce considerable concern regarding the effects that shell thinning may be having on reproductive success and status of these bald eagle populations.

## *Conclusion*

DDE residues in some eggs were of a magnitude that has produced shell thinning in experimental studies of other species. Significant shell thinning in most areas sampled causes concern for ultimate effects on reproductive success and populations. Dieldrin residues in the eggs from some areas could have an adverse effect on reproductive success.


## *Acknowledgment*

The authors wish to acknowledge the assistance of several individuals who aided us in various portions of this study. R. S. Christensen of WARF Institute, Inc. (P.O. Box 2037, Madison, Wis.) kindly provided the method used in the mercury analyses. Thair G. Lamont performed the mercury analyses reported here. Daniel W. Anderson and Joseph J. Hickey graciously provided unpublished eggshell data. Vernon D. Berns, Teryl G. Grubb, William C. Krantz, and Fred Lesser assisted in the egg collections.


See Appendix for chemical names of compounds discussed in this paper.

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# PESTICIDES IN WATER

## *Organochlorine Pesticide Residues in Water, Sediment, Algae, and Fish, Hawaii—1970-71* [1]

Arthur Bevenue, John W. Hylin, Yoshihiko Kawano, and Thomas W. Kelley

ABSTRACT

*Rainwater, drinking water, and nonpotable waters in Hawaii were sampled and found to contain chlorinated insecticide residues in the low parts-per-trillion range. Dieldrin, p,p'-DDT, and lindane were the pesticides most prevalent; pentachlorophenol was present in samples from a sewage fallout. The ratio of chlorinated pesticide residues in canal waters to residues in algae, sediment, and fish from the same canals was 1:4,000:9,000:32,000, respectively. According to proposed water quality standards, results of this study indicated that pollution of Hawaii's water by organochlorine pesticides does not occur to any significant degree.*

### *Introduction*

The study reported here was conducted to determine the extent of organochlorine pesticide contamination of water, sediment, algae, and fish in the State of Hawaii, which consists of eight major islands; in order of descending size, they are Hawaii, Maui, Oahu, Kauai, Molokai, Lanai, Niihau, and Kahoolawe. These islands comprise an area of 6,425 square miles (*1-3*).

The Hawaiian Islands have an abundance of potable water due to moisture-laden trade winds which blow southerly from a string of high-pressure areas to the north of the Island chain. As the trade winds strike the mountains of the Islands, rise in altitude, and are cooled, the water vapor is converted to rain. The amount of rainfall is related to the heights of the mountains. For example, the islands of Niihau and Kauai are at approximately equal latitudes; however, Niihau at an elevation of 1,281 feet has 26 inches of rainfall while Kauai at 5,170 feet has up to 482 inches. The unique formation of the Islands trap and store this rainwater; i.e., marine sediments and alluvial and talus sediments, deposited through the ages, have formed a relatively impermeable caprock around the Islands. At the highest elevations there may also be impermeable faults or dikes which impede the flow of rainwater—generally, however, rain falling at high elevations is rapidly absorbed into the porous volcanic basalt and percolates through the mountains to the water table where it accumulates to heights above sea level because of the caprock. Since fresh water is less dense than sea water, the fresh water in the water table literally floats on the sea water which has permeated the basalt. This relationship between the two waters was first discovered by Ghyben-Herzberg and is known as the Ghyben-Herzberg lense.

Because the major part of the State's population resides on Oahu and also for convenience, this Island was sampled much more extensively than the other Islands of the State. Subterranean Oahu may be classed as a water bank. The Board of Water Supply of the City and County of Honolulu taps this zone of fresh water with skimming tunnels, shafts, and artesian wells (*3*). It has been conservatively estimated that Oahu's current sources of potable water are sufficient to meet anticipated needs until the year 2000; more optimistic reports predict that these sources will provide sufficient water to meet demands over the next 90 years. About 1.8 billion gallons of water, as rain, falls on Oahu each day, 700 million gallons of which returns to the basin. At this time, Oahu uses about 430 million gallons each day.

Some areas of Oahu are only a few feet above sea level, and canals have been constructed to eliminate swamp-like areas and to receive surface runoff and storm-drain waters which eventually drain into the sea; much of this drainage into the canals originates from either industrial or residential areas.

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Hawaii produces about 75% of the world's pineapple crop and 25% of the United States' domestically grown sugar crop. Other agricultural activities include the commercial production of macadamia nuts, papaya, coffee, guava, passion fruit, avocados, bananas, taro, vegetable crops, beef cattle, dairy products, poultry, and swine. The sugar companies apply no insecticides to the land used for sugarcane production, but use primarily herbicides and rodenticides. The pineapple growers use insecticides, herbicides, and nematocides. Both use small amounts of plant growth regulators. Pasture lands are treated regularly with herbicides to control heavy brush foliage. In the other agricultural areas, the entire spectrum of pesticides is used. Termites are a constant problem in the islands, and commercial pest control operators use aldrin, dieldrin, chlordane, heptachlor, and pentachlorophenol in addition to the fumigants Vikane® (sulfuryl fluoride) and methyl bromide for their control. Numerous commercial formulations of insecticides, fungicides, and herbicides are sold locally for use in the average household.

Waters obtained for this study included 10 samplings of rainwater, 45 drinking waters, and 46 nonpotable waters.

Potable waters were sampled from 45 stations, including 28 wells, 4 shafts, 12 tunnels, and 3 springs on Oahu Island (Fig. 1). Nonpotable waters on Oahu were obtained from the Honolulu area on the leeward side and the Kaneohe-Kailua section on the windward side. Several swimming and surfing area were also sampled—Waialua Bay and Waimea Bay to the northwest and Kahana Bay in the northeastern area. In addition, two harbors, one industrial site, one sewage outfall, and two canals were sampled; sediment samples were also obtained from both canals (Fig. 2), and algae and fish specimens were obtained from one, the Ala Wai Canal. Nonpotable samples from the Island of Hawaii were from two populated areas (Hilo and Kona areas) and one unpopulated area of Punaluu (Black Sand Beach) (Fig. 3). Samplings from Kauai included five estuaries and one freshwater area (Fig. 3). The eight samples from Maui included water from a harbor, a pond, several streams, a golf trap at a resort, and a sump area which emptied excess drainage from a sugarcane field (Fig. 3).

## *Materials and Methods*

### WATER AND SEDIMENT

New, 1-gal glass bottles with metal screw caps and teflon liners were used to collect all water samples. Prior to use, these bottles and separatory funnels used in the analytical procedure were rinsed thoroughly with a solution of concentrated sulfuric acid and sodium dichromate, followed by rinsing with water, redistilled acetone, and redistilled hexane. All other glassware used in the analytical procedure was heat-treated for 16 hours at 200° C in an air-oven prior to use (*4*).

One-gallon grab samples of potable and nonpotable waters were obtained from various areas of the State, including representative samples of the 50 outlet stations of the drinking water supply for the City and County of Honolulu on the Island of Oahu. Rain-water samples were collected from different areas on Oahu during the period from December 1970 through February 1971.

FIGURE 1.—*Sampling sites for drinking waters, Oahu, Hawaii—1970-71*

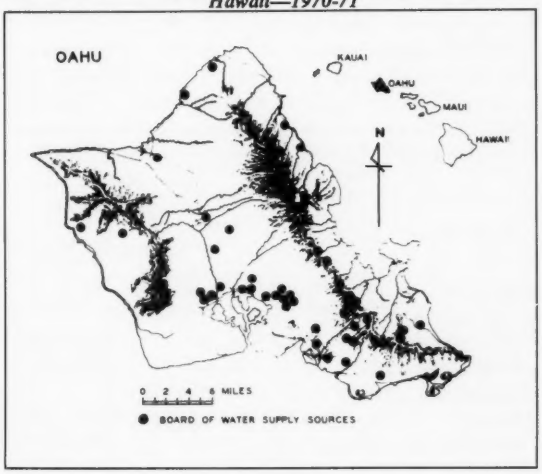


FIGURE 2.—*Sampling sites for nonpotable waters, Oahu, Hawaii—1970-71*

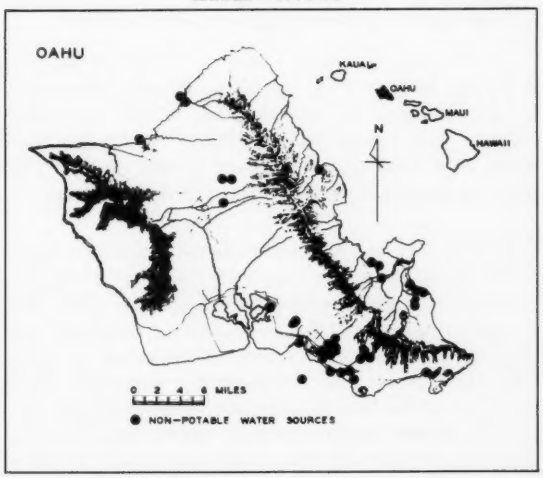

FIGURE 3.—*Sampling sites for nonpotable waters from the Islands of Hawaii, Kauai, and Maui—1970-71*

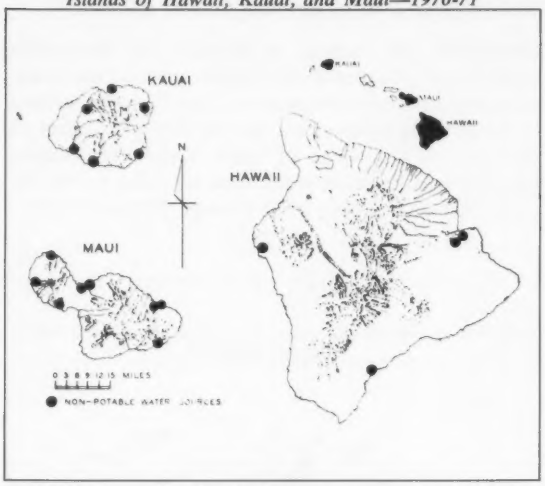


TABLE 1.—*pH and chloride ion concentration of water samples, Hawaii—1970-71*

| WATER SAMPLE | pH (RANGE) | CHLORIDE ION MG/LITER (RANGE) |
|---|---|---|
| Rainwater | 6.6 - 6.8 | 4 - 7 |
| Potable Water | | |
| Wells and Springs | 7.0 - 8.4 | 15 - 200[2](66) |
| Shafts and Tunnels | [1]6.8 - 9.4 | 13 - 78[2](28) |
| Nonpotable Waters[3] | | |
| Streams | 7.2 - 7.8 | 350 - 17,150 |
| Ponds | 7.3 | 1,400 - 5,680 |
| Bays | 7.4 - 8.1 | 2,450 - 19,525 |
| Canals | 7.1 - 7.8 | 10,300 - 14,800 |
| Lakes | 7.9 - 8.1 | 12,070 - 14,630 |
| Harbors | 6.7 - 8.1 | 13,000 - 19,460 |
| Basin | 7.9 | 18,970 |
| Lagoon | 8.2 | 19,180 |

[1] One sample of a total of 45 samples had a pH of 9.4 (sample was obtained from a lime-treated station).
[2] (Average) value.
[3] Average value for sea water is usually given as 18,980 mg/liter.

A portion of each water sample was used to determine pH and chloride ion concentration (Table 1). Total chloride was determined by titration of the acidified water with 0.1N or 0.01N silver nitrate solution and use of a Fisher Ag-AgCl, Model No. 36 titrimeter.

Sufficient water was removed from each sample to leave 3,000 ml of water in the bottle. Redistilled hexane (100 ml) was added to each sample, and the bottle was rotated at high speed for 1 hour on a roller-type jar mill. After mixing, each sample was allowed to stand until the hexane and water phases separated. Fifty milliliters of the hexane layer was removed with a volumetric pipette, transferred to a 125-ml round-bottom flask, and concentrated to a small volume using a rotary flash evaporator. The concentrate was transferred to a calibrated centrifuge tube and the final volume adjusted to 0.5 ml with the aid of a stream of nitrogen. Suitable aliquots, usually 10 $\mu$l, were applied to the gas chromatograph.

The sewage water sample was collected from an outfall discharge over a 24-hour day beginning at 7:00 a.m. December 14, 1970, and ending at 6:00 a.m. December 15, 1970. The sample was obtained at the sluice gate which was the last exposed point in the stream before flowing through the outfall sewer pipe. Samples were obtained hourly and then composited in proportion to hourly flow rates. The extraction procedure for the sewage water was modified in order to isolate any pentachlorophenol (PCP) in the water. Prior to the addition of hexane and the mixing step, the sample was adjusted to pH 13 with sodium hydroxide solution. The alkaline water was extracted three times with 100-ml portions of redistilled hexane in a separatory funnel; the hexane extracts were discarded. The sample was adjusted to pH 2 with concentrated sulfuric acid, 100 ml of redistilled hexane was added, the sample was mixed for 1 hour, and 50 ml of the hexane phase was concentrated as previously described.

The residue was concentrated to near dryness in a centrifuge tube, and excess diazomethane solution was added to convert any PCP in the sample to its ether derivative. Nitrogen was passed over the sample to remove excess diazomethane, the residue was made to a definite volume with hexane, and suitable aliquots were applied to the gas chromatograph.

A second sewage water sample, used for the analysis of chlorinated pesticides other than PCP, was cleaned up prior to analysis using the combined Florisil and silicic acid procedure of Armour and Burke (5). As noted by Armour and Burke, the Aroclors and aldrin are isolated in the first fraction of the silicic acid cleanup; the second fraction contains any remaining chlorinated pesticides except for dieldrin, which would be present in the 15% Florisil fraction. In the present survey, all data were compared with 10 available types of Aroclors. If any polychlorinated biphenyls were present in the examined samples, either they did not relate to the standard Aroclors used for comparison or were not detected; the latter was more often the case.

Sediment samples were obtained from several canals on the Island of Oahu with a dredge sampler or a 1-gal paint can. The solids content of the sediments was determined by air-drying a portion of each sample for 24 hours, followed by drying in an air-oven for 16 hours at 110° C. The wet sediment samples (50-100 g) were mixed thoroughly with equal weights of anhydrous sodium sulfate which had been previously heated 16 hours at 400° C; 100 ml of redistilled hexane was added

to each sample, the mixtures were shaken on a wrist-action shaker for 1 hour, and then allowed to stand until the suspended material settled. A measured amount of the hexane solution was removed and subjected to the Mills' Florisil cleanup procedure (*6*). The cleaned up extracts were concentrated, and aliquots of the concentrate were applied to the gas chromatograph.

### GAS CHROMATOGRAPHY

The following two gas chromatographs were used for analyzing the water and sediment samples: The first was a Varian-Aerograph Model 204, electron capture concentric tritium detector with ⅛″ x 6′ borosilicate glass column, with column temperature at 190° C, injector temperature at 210° C, detector temperature at 200° C, carrier gas—nitrogen, and flow rate—25 ml/min. The second was an F&M Model 810, electron capture parallel plate tritium detector with a ¼″ x 4′ borosilicate glass column, with column temperature at 190° C, injector and detector temperatures at 200° C, carrier gas—argon-methane (90:10), and flow rate—75 ml/min. Leeds and Northrup Speedomax H recorders, 1 mv full scale with a chart speed of 0.5″/min were used.

Four types of column packing were used, namely:

(1) 3% SE-30 on Chromosorb W, AW, DMCS, 80/100 mesh;
(2) 3% QF-1 and 2% DC-200 on Chromosorb W, AW, DMCS, 80/100 mesh;
(3) 4% SE-30 and 6% QF-1 on Chromosorb W, HP, 80/100 mesh; and
(4) 1.50% OV-17 and 1.95% QF-1 on Supelcoport, 100/200 mesh.

The retention times of the pesticides on these columns, relative to aldrin, are given in Table 2.

The limits of detectability of the pesticides ranged from about 0.05 ppt (lindane the most sensitive) to 0.5 ppt (DDT the least sensitive); dieldrin was detected at about 0.2 ppt. This is an approximate range only, because detection limits varied with the degree of purity of the water sample or the degree of success in cleaning up nonpotable water, sediment, and biota samples. The reported residue data are the amounts found by analysis; no attempt was made to correct the data based on recovery values obtained from fortified samples. Repeated attempts to obtain consistent and good recoveries of pesticides from samples spiked at the 1 and 2 ppt levels produced poor results. Efforts on confirmatory analyses by thin layer chromatography (TLC) were confined to samples containing at least 10 ppt of a particular pesticide. Confirmation by the "p" value procedure was difficult, if not impossible, in the residue range studied. Neither TLC nor "p" values were practical when working with residues in the low ppt range. Confirmation procedures were therefore limited to at least two two different types of gas chromatograph columns, a practice commonly used by many laboratories especially in preliminary survey work and where the amount of a sample may be limited.

### ALGAE AND FISH

The residue data on the algae and fish specimens were provided by Cynthia Schultz of the Department of Oceanography of the University of Hawaii and were obtained from the Ala Wai Canal during the same time period of this investigation. The cleanup procedure for these specimens was a modification of the procedure of Kadoum (*7*), whereby the extracts, previously partitioned with acetonitrile-hexane, were eluted through a micro-column of silica gel (Woehlm, Activity Grade No. 1, activated with 3% water) with a mixture of benzene-hexane (70:30). Analytical data were obtained with a MicroTek Model 220 gas chromatograph utilizing an electron capture detector.

TABLE 2.—*Retention times of pesticides in gas chromatographic columns relative to retention of time of aldrin, Hawaii—1970-71*

| Compound | 3% SE-30 | 3% QF-1<br>2% DC-200 | 4% SE-30<br>6% QF-1 | 1.50% OV-17<br>1.95% QF-1 |
|---|---|---|---|---|
| | Chromosorb W<br>AW, DMCS<br>80/100 Mesh | Chromosorb W<br>AW, DMCS<br>80/100 Mesh | Chromosorb W<br>HP<br>80/100 Mesh | Supelcoport<br>100/120 Mesh |
| Lindane | 0.43 | 0.57 | 0.54 | 0.64 |
| Heptachlor | 0.77 | 0.81 | 0.81 | 0.81 |
| Aldrin | 1.00 | 1.00 | 1.00 | 1.00 |
| Heptachlor epoxide | 1.26 | 1.47 | 1.43 | 1.62 |
| *p,p′*-DDE | 1.97 | 1.92 | 1.95 | 2.43 |
| Dieldrin | 2.26 | 2.19 | 2.19 | 2.60 |
| *p,p′*-DDD | 2.60 | 2.79 | 2.76 | 3.89 |
| *p,p′*-DDT | 3.46 | 3.36 | 3.44 | 4.69 |
| Pentachlorophenol ethyl ether | | | 0.57 | 0.55 |
| Pentachlorophenol methyl ether | | | 0.46 | 0.46 |

### *Results and Discussion*

The residue data on rainwater samples from Oahu are given in Table 3. Hawaiian rainwater contained *p,p'*-DDT, dieldrin, and lindane in the low ppt range. The only comparative data that could be found in the literature were from 1965 (*8,9*); the residues in the present study were much lower than the levels noted previously in the cities of Cincinnati, Coshocton, and Ripley, Ohio, (*8*) but similar to the amounts observed in Central England (*9*). It is possible that with increased restricted usage of chlorinated pesticides in the United States in the past 2 years, new measurements of rainwater in Ohio might show considerably lower quantities of these pesticides than reported in the earlier study.

TABLE 3.—*Organochlorine pesticide residues in 10 rainwater samples from Oahu, Hawaii, and in other studies*

| Compound | Hawaii 1970-71 | | Reported in Ohio 1965 (*8*) | | Reported in Central England 1965 (*9*) | |
|---|---|---|---|---|---|---|
| | Residues in PPT | | | | | |
| | Range | Average | Range | Average | Range | Average |
| *p,p'*-DDT | 1-13 | 3 | 70-340 | 187 | 2.4 | 3 |
| Dieldrin | 1-27 | 5 | [1] | | 3-16 | 9 |
| Lindane | 1-19 | 5 | 6-50 | 25 | 12-52 | 29 |

[1] Detected, but no values reported.

Residues in the drinking water samples were chlordane, DDT, dieldrin, and lindane and were in the low ppt range and about one-fifth or less the amounts noted in rainwater (Table 4). DDT was the predominant pesticide, appearing in 87% of the samples. Although extreme precautions were taken with the sampling procedures, pesticide contamination could have been present at the external source of sampling, because some of the stations are surrounded by sugarcane and pineapple growing areas or subdivision development projects.

The residues for drinking water were insignificant compared to the allowable amounts (Table 4) proposed by the Federal Committee to the Secretary of the Interior on Water Quality Criteria (*10*). The Committee has defined "permissible criteria" as "those characteristics and concentrations of substances in raw surface waters which will allow the production of a safe, clear, potable, aesthetically pleasing, and acceptable public water supply which meets the limits of drinking water standards after treatment." This Committee has also stated that it would be desirable to have no pesticides in drinking water supplies.

Ettinger and Mount (*11*) have stated that the use of waters for fish propagation must be considered in any set of acceptable State water quality criteria and that it has a bearing on drinking water standards. They have proposed the maximum stream allowance for certain pesticides (Table 4) which are one-tenth or less the amounts permissible by the Public Health Service. These allowances are greater than the amounts found in the local drinking water supply in Oahu. It is of interest to note that in 1962 the standards were revised to specify that the carbon chloroform extract (which is a measurement of synthetic chemicals in the environment including chlorinated insecticides) should not exceed 200 ppb (*12,13*). As late as 1967, an effort was made to include specific pesticides under these standards; however, it was pointed out that this could not be done in a legal sense, because pesticides were not classed in the "communicable disease category" (*14*).

TABLE 4.—*Organochlorine pesticide residues in 45 potable water samples from Oahu, Hawaii—February-May 1971*

| Compound | Range | Average | Percent of Samples | Maximum Permissible Criteria (*10*) | Maximum Reasonable Stream Allowances (*11*) |
|---|---|---|---|---|---|
| | Residues in PPT | | | | |
| Chlordane | 0.5-5.0 | 1.0 | 9 | 3,000 | 250 |
| *p,p'*-DDT | 0.6-2.2 | 1.0 | 87 | 42,000 | 500 |
| Dieldrin | 0.2-0.7 | 0.3 | 15 | 17,000 | 250 |
| Lindane | 0.06-0.4 | 0.2 | 4 | 56,000 | 5,000 |

Organochlorine pesticide residues in nonpotable waters were at the low ppt level, with *p,p'*-DDT representing the highest level (Table 5). In all areas sampled, dieldrin was consistently present and, in some instances, at a higher level than the other observed pesticides.

A crude attempt was made to classify the sampled areas into rural and urban sections of the State. The data show that the only major difference in residues in the waters was for dieldrin, which averaged about seven times higher in the urban areas (Table 6).

A detailed study was made of two canals and a stream, which were located primarily in the urban areas of Oahu, and a sewage outfall which received all sewage from the Honolulu area. One of the canals (Kapalama) and the stream passed through industrial areas. The water samples from the Kalihi stream were obtained near a wood treatment plant where, on the day of sampling, a heavy rain had drenched a large pile of pentachlorophenol-treated lumber. Drainage ditches from this lumber yard migrated to the sampled stream. The sample obtained from the ditch area nearest the lumber yard contained 1,143 ppt pentachlorophenol, whereas the sample obtained some distance from the yard and more a part of the stream contained 168 ppt pentachlorophenol, indicating a dispersion or diluent effect of the larger water area. Other pesticides, DDD, DDT, and dieldrin were also detected in the low ppt range, with dieldrin predominating in about 3-fold the quantities of DDT (Table 7). The sample from the sewage outfall contained 2,600 ppt pentachlorophenol, 198 ppt dieldrin, 107 ppt DDT, and 41 ppt lindane.

TABLE 5.—*Average amount and range of organochlorine pesticide residues in nonpotable waters, Hawaii—August 1970-February 1971*

| Island | No. of Samples | *p,p'*-DDE | *p,p'*-DDD | *p,p'*-DDT | Dieldrin | Lindane | Chlordane [1] |
|---|---|---|---|---|---|---|---|
| | | Residues in PPT | | | | | |
| Hawaii | 4 | — | — | 3.5 (3.2-3.8) | 5.5 (1.9-8.3) | — | |
| Kauai | 6 | — | — | 4.4 (3.4-7.1) | 1.1 (0.4-2.1) | — | |
| Maui | 8 | 0.7 (0.5-0.8) | — | 4.9 (2.6-6.8) | 1.6 (0.5-5.1) | 0.9 (0.2-3.4) | |
| Oahu | | | | | | | |
| Streams | 4 | 0.5 (0.2-0.8) | 0.1 (0.1) | 1.4 (1.0-1.7) | 1.5 (1.2-1.7) | 0.7 (0.4-1.1) | |
| Lakes | 5 | 0.3 0.1-0.5) | 7.8 (0.2-18.0) | 14.0 (0.2-64.0) | 2.0 (0.5-4.0) | 0.1 (0.1) | |
| Bays | 6 | 0.3 (0.1-0.6) | 3.6 (0.1-10.0) | 9.0 (0.4-41.0) | 1.0 (0.1-3.0) | 0.9 (0.3-2.0) | |
| Basin | 1 | — | — | 0.5 | 14.0 | — | |
| Harbors | 2 | — | — | 0.5 (0.5) | 3.5 (0.0-7.0) | — | |
| Lagoon | 1 | — | — | 0.5 | 11.0 | — | |
| Canals | 9 | 0.1 (0.0-1.0) | 2.4 (1.3-3.9) | 4.0 (1.0-7.1) | 13.0 (0.4-18.6) | 0.9 (0.3-2.0) | 6.9 (3.0-17.6) |

NOTE: — = not detected; figures in parenthesis = range.
[1] Chlordane analysis was not included in the early part of the study.

TABLE 6.—*Pesticide residues in waters from 13 rural and 24 urban areas in Hawaii—1970-71*

| Compound | Rural | | Urban | |
|---|---|---|---|---|
| | Range | Average | Range | Average |
| | Residues in PPT | | | |
| *p,p'*-DDE | 0.1-0.5 | 0.3 | 0.2-0.8 | 0.5 |
| *p,p'*-DDD | 0.1-10.0 | 3.1 | 0.8-18.0 | 3.4 |
| *p,p'*-DDT | 0.2-41.0 | 6.1 | 0.8-64.0 | 6.3 |
| Dieldrin | 0.1-4.0 | 1.2 | 0.3-19.0 | 8.4 |
| Lindane | 0.1-1.1 | 0.5 | 0.5-3.4 | 1.1 |
| Total chlorinated pesticides | | 11.2 | | 19.7 |

Extensive samplings of the waters of the two canals were made; these pesticide residue values are shown in Table 7. Again, the residues were in the low ppt range, with dieldrin predominating in quantity; however, the residues in the algae, fish, and sediments obtained from the same canals, were larger. Converting the total residues in the algae, sediment, and fish to parts per million places the values in the 0.1-1.0 ppm range, which is considerably lower than the 5.0 ppm DDT guideline value allowed in fish by Federal regulations. Converting dieldrin residue values found in the fish to parts per million gives values approximating the maximum permissible amounts. The amounts of chlordane and dieldrin found in the waters and the sediments and the pentachlorophenol residues observed in the sewage suggests that these pesticides originated primarily in the urban areas where many households and home builders use these compounds for the control of termites.

Summarizing the data in Table 7, the total amount of chlorinated insecticide residues in the waters of the two canals was the same at about 0.03 ppb; the residues in sediments (dry-weight basis) were 600 ppb. The total residues in the biota from the Ala Wai Canal on a fresh-weight basis were algae 130 ppb, small fish (guppies and mollies) 800 ppb, carnivore fish and detrital feeder fish each about 1,000 ppb. All three types of fish had similar amounts of total residue; however, the carnivore species contained a predominant amount of DDD, whereas the guppies, mollies, and detrital feeders contained predominant amounts of dieldrin.

The ratio of residues in the canal waters to those in the biota from the canals, assigning the value of 1 to water, were:

| | |
|---|---|
| Water | 1 |
| Algae | 4,300 |
| Sediment (wet-weight basis) | 9,000 |
| Small fish | 27,000 |
| Carnivore fish | 33,000 |
| Detrital feeder fish | 36,000 |

As noted by Gunther *et al.* (*15*) and others (*16,17*), published data on the solubility of pesticides in water are inconsistent and, at times, actually misleading and meaningless (Table 8). In waters containing salts, organic substances, and colloidal material, the solubility of a given pesticide may vary greatly, no doubt due to absorption or binding of the pesticide to suspended soil particles, plankton, and other types of matter in the water.

Pesticide residues found in natural water analyzed as received may vary considerably from residues found in the same water after it has been filtered through a glass fiber membrane. As stated by Walker (*18*), water containing suspended material appears to carry residues while water without this material may not contain measurable amounts of pesticides.

TABLE 7.—*Pesticide data on nonpotable waters from selected areas, Oahu, Hawaii—August 1970-February 1971*

| | Date Sampled | *p,p'*-DDE | *p,p'*-DDD | *p,p'*-DDT | Dieldrin | Lindane | Chlordane | PCP [1] |
|---|---|---|---|---|---|---|---|---|
| | | Residues in PPT | | | | | | |
| **ALA WAI CANAL** | | | | | | | | |
| Water | | | | | | | | |
| Station 1 | 8-12-70 | 1.0 | 2.0 | 1.0 | 5.0 | 1.0 | ([2]) | |
| | 2-18-71 | — | 1.3 | 1.6 | 9.6 | — | 9.4 | |
| Station 2 | 8-12-70 | — | 3.0 | 3.0 | 17.0 | 2.0 | ([2]) | |
| | 2-26-71 | — | 1.3 | 1.6 | 18.6 | 1.3 | 13.0 | |
| Station 3 | 8-12-70 | — | 3.0 | 2.0 | 16.0 | 2.0 | ([2]) | |
| | 2-18-71 | — | 2.6 | 1.6 | 0.4 | 0.3 | 4.8 | |
| | Average | 0.2 | 2.2 | 1.8 | 11.1 | 1.1 | 9.1 | |
| Sediment (dry-weight basis) | | | | | | | | |
| Station 1 | 2-18-71 | 100,000 | 220,000 | 150,000 | 100,000 | — | 720,000 | |
| Station 2 | 2-18-71 | 10,000 | 100,000 | 30,000 | 30,000 | — | 290,000 | |
| Station 3 | 2-18-71 | 10,000 | 40,000 | 40,000 | 100 | — | 125,000 | |
| | Average | 40,000 | 120,000 | 73,333 | 43,366 | — | 378,000 | |
| Biota (fresh-weight basis) | | | | | | | | |
| Algae | | 10,000 | 30,000 | 45,000 | 45,000 | — | — | |
| Fish | | | | | | | | |
| Guppy, Molly | June 1970 | 80,000 | 210,000 | 170,000 | 340,000 | — | — | |
| Carnivore (*Elops hawaiensis*) [3] | through Feb. 1971 | 182,000 | 581,000 | 101,000 | 141,000 | — | — | |
| Plankton and detrital feeder (*Chanos chanos*) [3] | | 298,000 | 149,000 | 159,000 | 486,000 | — | — | |
| **KAPALAMA CANAL** | | | | | | | | |
| Water | | | | | | | | |
| Station 1 | 2-9-71 | — | — | 7.1 | 16.4 | 1.0 | ([2]) | |
| | 2-16-71 | — | 3.9 | 4.7 | 10.2 | — | 3.0 | |
| | 3-1-71 | — | 3.9 | 6.4 | 18.0 | 0.5 | 4.4 | |
| | Average | — | 2.6 | 6.1 | 14.9 | 0.5 | 3.7 | |
| Sediment (dry-weight basis) | | | | | | | | |
| Station 2 | 2-19-71 | — | — | 50,000 | 370,000 | — | 255,000 | |
| Station 3 | 2-19-71 | 20,000 | 90,000 | 170,000 | 140,000 | — | 125,000 | |
| | Average | 10,000 | 45,000 | 110,000 | 255,000 | — | 190,000 | |
| **KALIHI STREAM** | | | | | | | | |
| Water (Industrial area) | | | | | | | | |
| Station 1 | 12-15-70 | — | — | 3.7 | 12.7 | — | ([2]) | 1.143 |
| Station 2 | 12-15-70 | — | 1.6 | 2.8 | 7.1 | — | ([2]) | 168 |
| | Average | — | 0.8 | 3.3 | 9.9 | — | | 655 |
| **SAND ISLAND OUTFALL** | | | | | | | | |
| Sewage (24-hr. composite discharge) | 12-14-70 | — | — | 107 | 198 | 41 | ([2]) | 2,600 |

NOTE: — = not detected.
[1] PCP = pentachlorophenol; analysis performed only on samples indicated.
[2] Chlordane analysis was not included in the early part of the study.
[3] Muscle tissue.

Water standards or "water quality criteria" are defined differently by different specialists; in fact, at this time, it is impossible to give an all-inclusive definition. For example, the publication of the Public Health Service on drinking water standards (*13*) states that "The Drinking Water Standards are regarded as a standard of quality which is generally attainable by good water quality control practices. Poor practice is an inherent health hazard. It has been the policy of the Committee to set limits which are not so low as to be impracticable nor so high as to encourage pollution of water.

"No attempt has been made to prescribe specific limits for every toxic or undesirable contaminant which might enter a public water supply. While the Committee is fully cognizant of the need for continued attention to chemical contamination of water, the standards are limited to recognized need. Standards for innumerable substances would require an impossible burden of analytical examination."

Another ill-defined area is toxicity data on fish. The publication "Water Quality Criteria" of the State of

California (*19*) states that "... the results by several investigators of the same pollutant may not compare closely. This wide discrepancy arises from variations in the species of fish or other organism used, its prior handling, the temperature, the season, the dissolved oxygen content, synergistic and antagonistic substances, the hardness and other mineral content of the water, and the time of exposure, ... sometimes vague terms such as toxic concentration of lethal dose are used without further definition. ... The effects of long-term exposures of fish populations to very low sublethal concentrations are not clearly understood."

It has been noted (*23*) that water analyses have limited meaning when evaluating the effects of a pesticide on animal populations. Johnson (*20*) concluded that water data alone on pesticides are an inadequate criterion for determining the relative danger or safety to the fish population in a given area; but it has also been stated that the very low concentrations observed in water may be important because natural mechanisms can concentrate residues many thousands of times. This is evident in the data obtained from the canal samples (Table 7).

Results given below from a survey of the literature indicate no consistency in the relation between residues found in various parts of a given ecosystem:

| *Study* | *Compound* | *Ratio of Residues in Various Parts of Ecosystem* |
|---|---|---|
| Macek (*21*)[1] | DDT | Water to fish-1:8,500 |
| Holden (*22*) | Dieldrin | Water to algae-1:1,000 |
| Woodwell *et al.* (*23*)[2] | DDT | Water to fish-1:20,000 |
| Johnson (*20*) | DDE | Water, sediment, and fish-1:1,500:20,000 |
| Hickey *et al.* (*24*)[3] | DDT, DDD, DDE | Sediment to fish-1:100 |
| Hannon *et al.* (*25*)[4] | DDT, DDD and DDE accounted for the greatest percentage of pesticide residues | Water, sediment, algae, fish-1:20:40:800 |

[1] Lab experiment—exposed fish to 3 ppt for 120 days.
[2] Reports data on an East Coast estuary.
[3] Reports data on an ecosystem of Lake Michigan.
[4] Residue data on a lake in South Dakota.

There is a general consensus that as many factors as possible should be examined in a given ecosystem. Pesticides are leached from soils by water, moved by erosion, and absorbed by mud-scavenging organisms (*23*); they are soluble in fats and oils; they tend to be concentrated in organic matter, algae, bacterial films, and slimes; and they can be suspended in colloidal forms (*22*). Most probably the food chain is the major source of pesticide contamination in fish (*21,26*), and, as stated by Eichelberger and Lichtenberg (*27*), there is no predictable safe level for pesticides in waters where food-chain buildup can occur.

TABLE 8.—*Reported water solubilities of some organochlorine pesticides at room temperature, 25° C*

| Compound | Gunther *et al.* (*15*) | Robeck *et al.* (*16*) | Bevenue and Beckman (*17*) |
|---|---|---|---|
| | Residues in PPB | | |
| Chlordane | [1] Insoluble | | |
| *p,p'*-DDD | [1] Insoluble | | |
| *p,p'*-DDT | [1] Insoluble<br>3.4<br>[2] 6 and 25 | [3] 16 and 40 | |
| Dieldrin | [2] 150 and 195<br>250 | [3] 140 and 180 | |
| Lindane | [2] 600 and 6,800<br>7,300 | [3] 500 and 6,000 | |
| Pentachlorophenol | | | [4] 14,000 to 19,000 |
| Sodium pentachlorophenate | | | 79,000 (pH 5)<br>4,000,000 (pH 8) |

[1] "Insoluble" = solubility up to about 1% or 10,000 ppm.
[2] Particle size 0.05 and 5.0 $\mu$.
[3] Particle size 0.04 and 5.0 $\mu$.
[4] At temperatures 20° to 30° C.

Several investigators have suggested that bottom muds and sediments should be given more attention in any pesticide study of water (*20,24,26*) and that these data should be combined with other available ecological information to give a good pesticide-pollution index.

In conclusion, it is emphasized that the present report is based on a preliminary survey of randomly selected samples. Future studies will include slick and strata sampling of the shoreline waters, seasonal sampling, an in-depth study of the sewage outfall, and, perhaps, concentrated sampling of areas in the State suspected of potentially higher pesticide residues. However, based on these preliminary data, on the present usage pattern of the pesticides studied, and comparison with the proposed water quality standards, pollution of Hawaii's waters by organochlorine pesticides does not occur to a significant degree.

See Appendix for chemical names of compounds discussed in this paper.

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# PESTICIDES IN SOIL

## *DDT Residues in Forest Floor and Soil After Aerial Spraying, Oregon—1965-68* [1]

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ABSTRACT

*One month after aerial application of DDT (12 oz/acre) to an eastern Oregon forest, 3 oz/acre of DDT residues (DDT, its isomers and metabolites—DDD, DDE, p,p'-DDT, and o,p'-DDT) were detected in the forest floor; 3 years later, the DDT content had decreased by more than 50%, and had not leached into the surface mineral soil.*

*At the time of spraying, water from two streams draining the sprayed area had a total DDT content of about 0.3 ppb. This low concentration decreased rapidly to levels below limits of analytical detection. No effect of the spraying was noted on soil microbial populations, nitrification rate, or amount of nitrate nitrogen in the soil.*

*Of the 12 oz of DDT applied per acre, about 26% reached the ground surface initially; and over 36 months, about 6% more was brought to the ground in litterfall. Thus, approximately one-third of the sprayed chemical reached the forest floor. The need for more efficient aerial methods of chemical application is evident.*

### *Introduction*

Only a few studies have been concerned with residues of DDT, its isomers and metabolites, in the forest environment. Woodwell (*41*) determined DDT residues in a forest in New Brunswick, Canada, which had been sprayed between 1952 and 1958 with a total of 4 lb/acre of DDT. He concluded that the maximum residue persistence time in forest soil would be 10 years and that *o,p'*-DDT was leached into the subsoil. Woodwell and Martin (*42*) reported that DDT residues in heavily sprayed forest soils in Maine and New Brunswick increased over a period of 3 years after final spraying. These authors hypothesized that DDT residues persist in the forest canopy and are carried to the soil by rain and litterfall.

Yule (*43*) stated, however, that Woodwell's hypothesis of differential weathering and preferential retention of *o,p'*-DDT by New Brunswick forest soils is untenable. He concluded from a study in the same locality that about 16% of the DDT originally applied still remained in surface soils after almost 20 years, but mainly in the form of the most toxic isomer, *p,p'*-DDT. He further demonstrated that the acidic, highly organic, forest surface soils held these DDT residues unavailable in toxic amounts to soil insects.

DDT residues were also measured in a northern Pennsylvania forest soil, 380 days after aerial spraying at a rate of 0.5 lb/acre (*9*). The only environmental change reported was a significant accumulation of DDT in the forest floor and surface soil. One year after spraying, no measurable increase in DDT residues was noted in fish, crayfish, or stream sediments. Belyea (*4*) studied DDT residues in soils and a related food chain in northern Maine forests. He concluded that DDT would disappear from these soils in 10-12 years. In western Washington, DDT was applied to the surface of a gravelly soil beneath a stand of Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] at 0.5 and 5.0 lb/acre (*29*). Regardless of application rate, less than 1% of the DDT applied leached through the surface soil.

In 1965, an opportunity to further study DDT residues in forests resulted from a spray project conducted by the U. S. Forest Service between June 10 and July 1 to control a serious outbreak of the Douglas-fir tussock moth (*Hemerocampa pseudotsugata* McD.) in eastern Oregon. Helicopters were used to spray 66,000 acres of forest with an insecticide formulation of 0.75 lb of technical grade DDT dissolved in 0.94 qt of hydrocarbon solvent and sufficient No. 2 fuel oil to make 1 gal of solution at 60° F; the application rate was 12 oz/acre.

[1] From the Pacific Northwest Forest and Range Experiment Station, U. S. Department of Agriculture, Forest Service, Corvallis, Oreg. 97330.

A number of public agencies have already conducted surveillance and monitoring activities to determine residues in fish and wildlife, cattle, and forage, and to ascertain public health effects from the spray project (*10,35*). The present study reports observations of the persistence of the applied DDT in the forest floor and soil and some related effects for the first 3 years after the spray project.

The area studied was along a 1-mile transect in the Malheur National Forest of eastern Oregon. Elevation of the area is 5,700 feet. The subhumid continental climate includes dry, warm summers (>100° F maximum temperature) and cold winters (−20° F minimum temperature). The daily range of temperatures in summer is often 40 to 50 degrees and the monthly range may exceed 60 degrees. Annual precipitation averages about 20 inches, one-third to one-half of which is snow. Most moisture available to plants is stored in the soil at the beginning of the growing season, and by midsummer soils become very dry; summer flow in small streams is intermittent.

The soil of the study area, representative of perhaps several million acres of eastern Oregon forest land, is tentatively identified as a member of the Klicker series. This is a well-drained, moderately fine-textured, forested soil developed in residuum from basalt bedrock; small fragments of the basaltic parent material occur throughout the solum, and rock outcrops are common throughout the area. The A horizon, which may contain volcanic ash, ranges in texture from silt loam to silty clay loam, with the percent clay increasing gradually with soil depth. The soils are slightly acidic throughout the solum which ranges in depth from 15 to 35 inches. Permeability is moderate, and surface runoff is medium. Major tree species in the study area which partially determine the amount of litter and duff on the forest floor are ponderosa pine [*Pinus ponderosa* (Laws).], White fir [*Abies concolor* (Gord. & Glend..) Lindl.], and Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco].

### *Sampling Procedures*

Five 1/10-acre plots were established along the transect nearest to equidistant points where maximum uniformity of stand composition and density could be found. Within each of the five plots, four sampling points were randomly selected. At each point, the forest floor over a 4-sq-ft area was carefully removed, and 1-qt samples of soil were collected at each of two depths, 0 to 3 inches and 3 to 6 inches, in step-like trenches. Extreme care was taken to avoid contaminating the lower sample with material from above, and all tools were cleaned frequently with acetone. Samples were placed in new 1-qt paper freezer containers, stored during the day in portable cooler chests, and frozen the same day they were collected. Samples of forest floor and soil were collected prior to the spray project, 1 month after the spraying, and at 1-year intervals. Litterfall, throughfall precipitation, and water samples from streams were collected every 6 months.

Eight trays, each with a surface area of 10.9 sq ft, were randomly placed throughout each sample plot to collect litterfall, and four 1-gal containers fitted with funnels having openings approximately 1 sq ft in size were randomly located in each sample plot to collect precipitation. Water samples from the east and west forks of Rattlesnake Creek within 50 feet of their confluence were taken in 1-gal containers, submerged just deep enough to prevent undue disturbance of bottom sediments.

### *Analytical Procedures*

Soil samples were air-dried, ground, passed through a 10-mesh sieve, mixed, and subsampled. For samples intended for microbial analysis, the sieve was cleaned with 30% ethanol and flamed between collections of each sample. Frozen litter and forest floor samples were chopped with dry ice, mixed, and subsampled. All samples, including water, were stored at 0° F until extracted.

#### EXTRACTION

Soils: A 100-g subsample was extracted with 41:59 hexane:acetone (azeotropic) in a Soxhlet extractor for 16 hours (*27*).

Litter and forest floor: A 25-g subsample was extracted with acetone in a Soxhlet extractor for 16 hours.

Water: Volumes up to 4,000 ml were extracted with hexane in a continuous-cycling liquid-liquid extractor for 16 hours.

#### CLEANUP

The soil and litter extracts were transferred to separatory funnels. Water was added to form a 2:1 water-acetone solution. The pesticides were partitioned into hexane by shaking with three 100-ml aliquots of hexane (*17*).

The hexane extracts of soil, litter, and water were dried with anhydrous sodium sulfate, evaporated to a small volume (5- to 10-ml), and transferred to a 15-g Florisil column (*40*). The pesticides were eluted from the column with 100 ml of 1:3 dichloromethane:hexane. Dichloromethane was removed by evaporation, and samples were transferred to volumetric flasks for analysis.

#### ANALYSIS

The concentration of DDE, *o,p'*-DDT, DDD, and *p,p'*-DDT was quantified in a MicroTek 2000 MF gas chromatograph with a 130-mc tritium electron capture detector. This system gave good individual peak resolution at the following retention times: DDE, 5.2 minutes;

*o,p'*-DDT, 6.8 minutes; DDD, 8.0 minutes; and *p,p'*-DDT, 9.5 minutes. Other operating parameters were:

| | | |
|---|---|---|
| Column: | Pyrex glass, 180 cm x 2 mm i.d., packed with 5% QF-1 (0.7 of length) and 5% DC-11 (0.3 of length) on 60/80 mesh Gas Chrom Q, preconditioned for 48 hours at 220° C. | |
| Temperature: | Column | 185° C |
| | Detector | 190° C |
| | Injector | 205° C |
| Carrier gas: | Nitrogen at 30 ml/min | |

Minimum residue levels for quantitative determinations were 0.001 ppm for soil, 0.01 ppm for forest floor and litter, and 0.01 ppb for water. Average percent recovery and range for DDT isomers and metabolites were as follows:

| Form of DDT | Soil (ppm) | Forest Floor and Liter (ppm) | Water (ppb) |
|---|---|---|---|
| DDE | 99(92-103) | 97(93-100) | 99(98-100) |
| *o,p'*-DDT | 82(71-99) | 99(96-100) | 98(97-100) |
| DDD | 82(78-91) | 85(80-94) | 94(93-95) |
| *p,p'*-DDT | 97(92-100) | 94(90-97) | 99(98-100) |

NOTE: ( ) = range.

### CONFIRMATION

It is most necessary to positively identify any apparent DDT determined by gas-liquid chromatography (GLC), especially in samples of materials to which no known DDT application was made. A number of industrial pollutants are similar to DDT in structure and properties and can interfere with the detection or identification of DDT (*19,22,28,30,31*); some naturally occurring plant or soil substances may also be potential sources of analytical error in determining the presence of chlorinated hydrocarbon compounds (*14,20*). To confirm apparent DDT residues in this study, about half the samples were analyzed by GLC with a chloride-specific, microcoulometric detection system (Infotronics Instrument Corp.). This step confirmed that substances with the same retention time as the DDT standards detected by the electron capture detector did contain chlorine, but did not rule out the possible misinterpretation of polychlorinated biphenyls (PCB's) as DDT isomers and metabolites. Therefore, all samples analyzed with the microcoulometric detector were hydrolyzed with alcoholic potassium hydroxide which would chemically alter DDT and DDD, but not PCB's (*17*). Hydrolyzed samples were then re-analyzed by both electron capture and microcoulometric detection systems. DDD, *o,p'*-DDT, and *p,p'*-DDT peaks disappeared after hydrolysis, indicating that PCB's were not present in detectable qualities and that the quantitative measurement of DDT isomers and metabolites by the electron capture detection system was correct.

The mass spectrophotometer provides the most positive means of identifying pesticides in biological samples; but in this study, only a few forest floor samples contained sufficient DDT to use this instrument. Two composite samples of forest floor from two different plots were extracted and purified for this particular analysis. The DDT isomers and metabolites were separated by chromatography of the final hexane extract on 500-$\mu$ silica gel H thin layer plates developed with 4:96 benzene:hexane. DDT standards were co-chromatographed on both edges of the 20- by 20-cm plates. After development, a 15-cm strip in the middle of the plate was covered, and the DDT standards were located by spraying the edge of the plate with 0.5% silver nitrate and exposing to UV light for 15 minutes. The *o,p'*-DDT, *p,p'*-DDT, and DDE were scraped from the appropriate section of the center of the plate, extracted from the silica gel with hexane, and analyzed by gas chromatography (electron capture detector). The pesticides separated by the thin layer method had the same retention times as the standards.

Extracts containing the individual pesticides were introduced into a Model CH 7 (Varian Mat. Bmg. H.) mass spectrometer with a direct inlet probe. The mass spectra for *o,p'*-DDT, *p,p'*-DDT, and DDE isolated from the forest floor samples agreed with spectra of appropriate standards and with published spectra (*34*). Sample spectra compared with published PCB spectra (*3*) indicated no PCB's present in the isolated pesticides. All confirmation steps gave positive evidence that the substances isolated and measured were indeed DDT isomers and metabolites and that PCB's were not present in detectable quantities.

### MICROBIAL ANALYSIS

The number of bacteria in soil was estimated by plating sterile tap water dilutions of soil on sodium albuminate agar; mold counts were made on plates of peptone-glucose-acid agar (*37*). In each case, five plates were poured of each dilution: 1:50, 1:500, and 1:5,000 for molds; 1:5,000, 1:50,000, and 1:500,000 for bacteria. Mold colony counts were made on plates showing approximately 30 to 100 colonies after 3 days' incubation; major genera were differentiated as mucors, *Penicillium*, and *Aspergillus* after 3 to 7 days. Total bacteria and *Streptomyces* were counted on plates showing colonies in the range of 50 to 300 after 10 to 14 days' incubation; *Streptomyces* were differentiated and their numbers expressed as a percentage of the total count. Incubation was 28° C.

Nitrite and nitrate were determined colorimetrically by the diazotization (*2*) and phenoldisulfonic acid (*18*) methods, respectively. For the nitrification study, 200 ppm N was added as ammonium sulfate to 100 g of soil (oven-dry basis) in 1-pt bottles. Moisture was adjusted

to 50% of water-holding capacity, and the bottles were capped with polyethylene film and incubated for 30 days at 28° C. Distilled water sufficient for a 1:5 dilution was then added, and the samples shaken for 15 minutes. After pH was measured, nitrite and nitrate in the supernatant were determined.

## *Results and Discussion*

### FOREST FLOOR SAMPLES

A very small amount (0.13 ppm) of "apparent" total DDT residues (*p,p'*-DDE, *p,p*-DDD, *o,p'*- and *p,p'*-DDT) were found in prespray samples of the forest floor (Table 1); this was not confirmed as DDT, its isomers and metabolites by means other than GLC because of its insignificant contribution (<0.01 oz/acre) to the totals found after spraying. One month after spraying, concentration of total DDT in the forest floor was slightly more than 7.5 ppm (Table 1), or 3.08 oz/acre (Fig. 1). Thus, an estimated 26% of the applied DDT (12 oz/acre) reached the forest floor shortly after spraying. DDT residues in the forest floor decreased steadily with time, and at the end of 3 years, more than half the DDT originally added had disappeared. Volatilization, chemical or photochemical degradation, and bacterial decomposition are possible removal mechanisms (*12*).

TABLE 1.—*Concentration of DDT isomers and metabolites in the forest floor before and after aerial spraying, Oregon—1965-68*

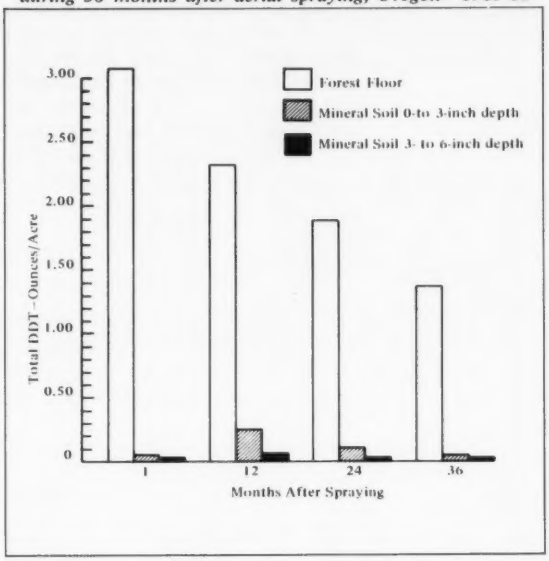
| Months after Spraying | Residues in PPM on a Dry-Weight Basis [1] | | | | |
|---|---|---|---|---|---|
| | *p,p'*-DDE | *o,p'*-DDT | *p,p'*-DDD | *p,p'*-DDT | Total DDT |
| 0 | .008 | .025 | .008 | .089 | .130 |
| 1 | .190 | 1.294 | .348 | 5.708 | 7.540 |
| 12 | .214 | .957 | .352 | 3.914 | 5.437 |
| 24 | .298 | .584 | .198 | 3.332 | 4.412 |
| 36 | .096 | .473 | .114 | 2.641 | 3.324 |

[1] Each value for DDE, DDD, *o,p'*- and *p,p'*-DDT represents the average of duplicate determinations on 20 replicate samples. The relationship between concentrations of all isomers and metabolites and months after spraying is negatively linear and significant at the 5% probability level.

### SOIL SAMPLES

DDT did not leach from the forest floor to underlying mineral soil. Apparent total DDT in prespray samples was 0.006 ppm (Table 2, or 0.05 oz/acre (Fig. 1) at the 0- to 3-inch depth; at the 3- to 6-inch depth, total DDT concentration was 0.002 ppm, or 0.02 oz/acre. One month after spraying, these levels had not changed, indicating that the forest floor effectively intercepted the spray solution. One year after spraying, the residue level of total DDT in soil at the 0- to 3-inch depth was 0.26 oz/acre; at the 3- to 6-inch depth, it was 0.05 oz/acre. This small difference in residues 1 month after spraying and 1 year later was attributed to the physical action of soil animals and, most probably, to minor, unavoidable contamination during sampling. DDT has a solubility in water of only about 1 ppb (*7*), and thus, does not leach readily in soil (*16,29,33*). At the end of the second year, total DDT at the upper and lower soil depth has decreased to 0.11 and 0.03 oz/acre, respectively, and by the end of 3 years, was at prespray levels.

FIGURE 1.—*Total DDT in forest floor and mineral soil during 36 months after aerial spraying, Oregon—1965-68*




### LITTERFALL SAMPLES

DDT in litterfall totaled 0.73 oz/acre over the 3-year sampling period, about 6% of the original application (Fig. 2). DDT concentration decreased with time at a greater rate than it did in the forest floor and soil (Table 3), suggesting that photochemical decomposition and volatilization may be effective mechanisms of chemical degradation in tree canopies exposed to sunlight. DDT concentration is also reduced in successive litterfall samples because of the constantly decreasing proportion of needles and twigs originally subjected to the spray. The contribution of DDT from litterfall to the forest floor after spraying did not contribute strongly to total amount observed. Total loss of DDT from the forest floor over 3 years amounted to 2.46 oz/acre, more than three times the amount brought down in litterfall over the same period.

### THROUGHFALL PRECIPITATION SAMPLES

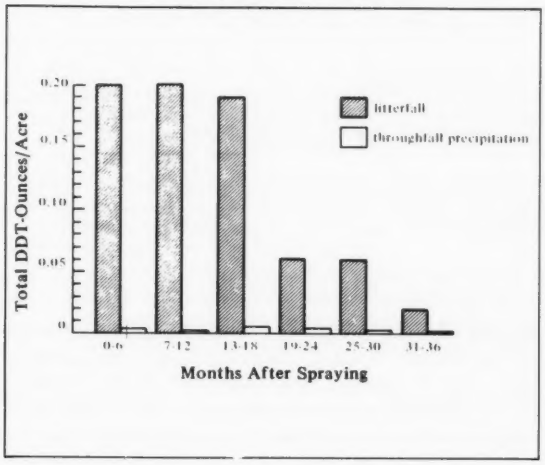
Additions of DDT to the forest floor by throughfall precipitation were insignificant—0.02 oz/acre for the 3-year period following application (Fig. 2) Concentrations varied with season (summer-fall vs. winter-spring) and, in general, showed a gradual decrease with time (Table 4). DDT concentrations in samples representing the dry summer and fall months were approximately three times greater than those for the wet winter-spring

TABLE 2.—*Concentration of DDT isomers and metabolites in surface soil before and after aerial spraying, Oregon—1965-68*

| Months after Spraying | Residues in PPM on a Dry-Weight Basis [1] | | | | |
|---|---|---|---|---|---|
| | *p,p'*-DDE | *o,p'*-DDT | *p,p'*-DDD | *p,p'*-DDT | Total DDT |
| 0- to 3-inch depth | | | | | |
| 0 | .001 | .002 | — | .003 | .006 |
| 1 | .001 | .001 | — | .004 | .006 |
| 12 | .003 | .005 | — | .021 | .029 |
| 24 | .001 | .002 | — | .009 | .012 |
| 36 | — | .001 | — | .005 | .006 |
| 3- to 6-inch depth | | | | | |
| 0 | — | .001 | — | .001 | .002 |
| 1 | — | .001 | — | .001 | .002 |
| 12 | — | .002 | — | .004 | .006 |
| 24 | — | .001 | — | .002 | .003 |
| 36 | — | .001 | — | .001 | .002 |

NOTE: — = not detected.
[1] Each value for DDE, DDD, *o,p'*- and *p,p'*-DDT represents the average of duplicate determinations on 20 replicate samples.

FIGURE 2.—*Total DDT brought to forest floor in litterfall and throughfall precipitation during 36 months after aerial spraying, Oregon—1965-68*




season. Precipitation samples for the 13- to 18-month period after treatment contained higher DDT concentrations than expected relative to the amount of rainfall for the period and the concentrations found at 6 and 30 months. However, the DDT levels, their seasonal variations, and the total range in concentrations found in this study are consistent with normal climatological variations and similar to those reported for other regions (*1,36,39*).

TABLE 3.—*Concentration of DDT isomers and metabolites added to the forest floor in litterfall after aerial spraying, Oregon—1965-68*

| Months after Spraying | Residues in PPM on a Dry-Weight Basis [1] | | | | |
|---|---|---|---|---|---|
| | *p,p'*-DDE | *o,p'*-DDT | *p,p'*-DDD | *p,p'*-DDT | Total DDT |
| 0-6 | .66 | 1.57 | .44 | 8.65 | 11.32 |
| 7-12 | .19 | 1.65 | .30 | 8.18 | 10.32 |
| 13-18 | .13 | 1.06 | .22 | 5.71 | 7.12 |
| 19-24 | .15 | 1.07 | .26 | 6.01 | 7.49 |
| 25-30 | .09 | .62 | .13 | 3.08 | 3.92 |
| 31-36 | .07 | .47 | .10 | 2.44 | 3.08 |

[1] Each value for DDE, DDD, *o,p'*- and *p,p'*-DDT represents the average of duplicate determinations on 20 replicate samples. The relationship between concentrations of DDT isomers and metabolites and months after spraying is negatively linear and significant at the 5% probability level in all cases.

TABLE 4.—*Concentration of DDT added to the forest floor in throughfall precipitation after aerial spraying, Oregon—1965-68*

| Months after Spraying | Precipitation [1] (mm) | Total DDT Residue [2] (ppb) |
|---|---|---|
| 0-6 | 162 | .176 |
| 7-12 | 212 | .075 |
| 13-18 | 185 | .364 |
| 19-24 | 455 | .066 |
| 25-30 | 110 | .103 |
| 31-36 | 241 | .036 |

[1] Rainfall level extrapolated from monthly climatological data for Burns, Oregon, using Mean Annual Precipitation Isohyetal Map, U. S. Weather Bureau River Forecast Center, Portland, July 1964.
[2] Total DDT residue includes *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDD and *p,p'*-DDT. DDE residue accounted for an average 6.58% of total DDT residue and showed no statistically significant change with time.

At the end of 3 years, DDT concentrations in throughfall precipitation had decreased appreciably, but still were 5 to 10 times greater than levels found in samples from an untreated forested area in western Oregon; however, the total amount of DDT brought down over this period in throughfall precipitation was negligible compared with that part of the intended application that initially reached the forest floor or was deposited in litterfall. Thus, throughfall precipitation was not a significant factor in determining the fate of applied DDT or in maintaining DDT concentrations in the forest floor.

### DDT IN STREAMWATER SAMPLES

Streamwater was monitored in Rattlesnake Creek immediately above the confluence of the east and west forks, both of which flow from the sprayed area. The maximum total DDT concentration found over a period of 3½ years after spraying was 0.277 ppb; this was in a sample taken a few hours after spraying (Table 5). This level was similar to those reported from North Carolina (*15*) and northeastern California (*5*) and less than those from northern Pennsylvania (*9*) and New Brunswick (*44*). Most samples, including those taken 3½ years after the spraying, contained concentrations of DDT near the lower limit of detection (0.01 ppb).

TABLE 5.—*Total DDT content of streamwater flowing from sprayed area—before treatment and during 3 years after treatment, Oregon—1965-68*

| Date | Days from Time of Spraying | Total DDT Residues in PPB | |
|---|---|---|---|
| | | Rattlesnake Creek East Fork | West Fork |
| 1965 | | | |
| 5/24 | −30 | | |
| 6/19 | −4 | — | — |
| 6/23 | 1 | .104 | .277 |
| 7/14 | 21 | .031 | .022 |
| 8/26 | 64 | .028 | .015 |
| 11/17 | 147 | .014 | — |
| 1966 | | | |
| 6/7 | 349 | | — |
| 7/19 | 391 | .010 | |
| 11/9 | 505 | | |
| 1967 | | | |
| 7/4 | 742 | — | — |
| 11/7 | 869 | .032 | .010 |
| 1968 | | | |
| 7/16 | 1,131 | | |
| 11/12 | 1,251 | .010 | |

NOTE: — = not detected.
Blank = levels of DDT isomers and metabolites less than 0.01 ppb but greater than 0.002 ppb.

Surveillance operations by the Bureau of Sport Fisheries and Wildlife (*25*) indicated that the DDT spraying had little effect on the waters and organisms of Malheur Lake, toward which Rattlesnake Creek flows. Levels of total DDT accumulation in the food chain of Rattlesnake Creek were very low in all components of the sampled community (*8*).

## MICROBIAL SOIL PROPERTIES AND NITROGEN RELATIONS

The small amount of DDT in the top 6 inches of mineral soil had no significant effect on microbial populations, soil nitrification rate, or amount of nitrate nitrogen (Table 6). A number of findings similar to these are found in the literature; these reports, however, are based on laboratory studies in which DDT was added to soil at extremely high rates—50-2,000 lb/acre (*13,21,24,26,32*). Effects of pesticide residues on microbes in agricultural soils are usually negligible when the chemicals are used at recommended field rates (*6, 11,23*). Such field rates were usually much greater than those encountered in this study. Thus, it may be concluded that the small amount of total DDT residue in soil found after low-volume aerial spraying to control insects is not hazardous to soil microbes or their role in maintaining soil fertility.

## FATE OF AERIALLY APPLIED DDT

Of a total aerial application of 12 oz of DDT per acre, 26% reached the forest floor initially, 6% was brought to the forest floor in litterfall over a 3-year period, and a fraction of 1% of the total was washed from the tree canopy over 3 years (Table 7). Thus, about one-third of the total application reached the forest floor.

TABLE 6.—*Soil microbial populations, nitrate nitrogen content, and nitrification rate before treatment and during 24 months after aerially spraying with DDT at 12 oz/acre, Oregon—1965-68*

| Variable and Unit of Measurement | Soil Depth (inches) | Months after Aerial Spraying [1] | | | |
|---|---|---|---|---|---|
| | | 0 | 1 | 12 | 24 |
| Total bacteria—millions/g of soil | 0-3 | 2.51 | 2.81 | 3.46 | 7.58 |
| | 3-6 | 1.83 | 2.05 | 4.04 | 4.51 |
| Streptomyces—percent of total bacteria | 0-3 | 15.25 | 23.63 | 27.25 | 63.81 |
| | 3-6 | 13.13 | 19.50 | 35.56 | 34.00 |
| Total molds—thousands/g of soil | 0-3 | 338.19 | 302.88 | 464.69 | 168.31 |
| | 3-6 | 93.88 | 33.88 | 323.31 | 35.06 |
| Penicillia—percent of total molds | 0-3 | 78.23 | 94.46 | 95.06 | 62.72 |
| | 3-6 | 77.10 | 68.45 | 82.78 | 68.45 |
| Nitrate nitrogen in soil—ppm | 0-3 | 58.00 | 40.94 | 7.00 | 17.50 |
| | 3-6 | 5.81 | 4.31 | 1.63 | 2.13 |
| Nitrification of added ammonium sulfate—percent of total added | 0-3 | 9.59 | −.56 | −.50 | −.17 |
| | 3-6 | .27 | .04 | −.26 | −.13 |

[1] Results of regression analysis indicated no significant relation between soil DDT content and any of the variables measured at the 5% probability level.

TABLE 7.—*Total DDT deposited on the ground surface (forest floor) during 3 years after aerially spraying of DDT at 12 oz/acre, Oregon—1965-68*

| Source of DDT at Ground Surface | Total DDT | |
|---|---|---|
| | oz/acre | Percent of Total Applied |
| Initial deposit from spraying | 3.08 | 25.66 |
| Total deposit during 3 years from: | | |
| Litterfall | .74 | 6.17 |
| Throughfall precipitation | .02 | .01 |
| Total, all sources | 3.84 | 31.84 |

Because this study did not include direct measurement of the amounts of DDT that reached the forest canopy, the extent of chemical loss from drift during spraying or by volatilization or degradation in the canopy after spraying cannot be assessed. In a study in Arizona, less than 50% of aerially sprayed insecticides were deposited on the agricultural target during summer months (*38*); in the same study, the distance from the spray aircraft to the target was inversely correlated with amount of on-target chemical application. Aircraft spraying forest lands must fly at far greater heights than those operating over level agricultural fields. Thus, the comparatively low amount of on-target application suggested by the present study is not surprising. This finding reaffirms that efficient methods of aerial spraying must be developed in order to avoid great loss of chemical to nontarget areas.

See Appendix for chemical names of compounds discussed in this paper.

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# GENERAL

## *Decay of Parathion and Endosulfan Residues on Field-Treated Tobacco, South Carolina—1971*

Julian E. Keil,[1] C. Boyd Loadholt,[2] Bob L. Brown,[3] Samuel H. Sandifer,[1] and Wayne R. Sitterly [4]

ABSTRACT

*Parathion and endosulfan were applied three times at rates of 1.5 and .5 lb/acre, respectively, to field tobacco in South Carolina in an effort to determine the time required for these pesticides to degrade to "zero" residue levels. The maximum times were estimated to be 7 days for parathion and 10 days for endosulfan. During the study period, weather was characterized by high rainfall and temperatures averaging 80° F.*

### *Introduction*

The recent increased use of organophosphate pesticides such as parathion as substitutes for the restricted chlorinated hydrocarbons has revived concern about residues of these compounds. Interest was further stimulated by the reported cluster of parathion poisonings among North Carolina tobacco workers in 1970 (J. I. Freeman, *personal communication*).

Cowart *et al.* (*2*) in measuring the hydrolysis rate of parathion reported that 85% remained undegraded after 1 week, 75% after 2 weeks, and 17% was still undegraded at 6 weeks. Maier-Bode (*3*), however, reported that the question of how long parathion residues remained in and on food plants has been answered. He concluded that parathion as a spray or powder is absorbed into plant tissues where metabolism occurs; any remaining surface residues are rapidly broken down by photolysis of the sun or evaporated into the atmosphere. Maier-Bode advised that German law requires a waiting time of 14 days between parathion application and harvest to reduce residues to levels nonhazardous to human health. He also suggested that rain during this waiting period does not significantly affect the residue level.

The U. S. Department of Agriculture has long suggested that workers entering tobacco fields within 5 days after application of parathion be protected against skin contact by use of protective clothing (*1*).

The experiment reported here was designed to observe the decline with time of levels of parathion normally applied to field tobacco. The ultimate goal was to estimate and verify the safe interval suggested by USDA for entering fields after parathion treatment.

Endosulfan, a chlorinated hydrocarbon insecticide still registered for use on tobacco, was included as another treatment and also mixed with parathion to assay decay interaction of the two chemicals.

### *Methods and Procedures*

Cokers 319 variety tobacco was planted on April 12, 1971. Plots consisting of three 12-foot rows were randomly selected for treatment with parathion, endosulfan, or parathion in combination with endosulfan or as appropriate controls. Each treatment or control plot was replicated four times in a completely randomized design for a total of 16 plots. Guard rows were used to reduce pesticide drift. Parathion and endosulfan were applied as sprays at rates of 1.5 and .5 lb active ingredient (A.I.) per acre, respectively, on June 8, 21, and July 8, 1971.

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Twelve foilage sample collections were made at times indicated in Table 1 and Fig. 1 and 2. Each time, 25-g, field-weighed samples were secured from the center alley of each plot from the foliage of two plants at locations approximately one-half the plant height. The samples were placed in acetone-washed, oven-dried, 1-pint containers.

Rainfall data, shown in Fig. 1 and 2, were obtained as recorded at the Clemson University Truck Experiment Station, and temperature information was secured from the U. S. Weather Bureau.

Since all plots were observed at 12 different times, the statistical analysis computed (Tables 2 and 3) was for a split plot in time where the whole plots were in a completely randomized design.

### *Analytical Procedures*

To each 25-g sample of tobacco, 50 ml of nanograde hexane and 5 g of anhydrous sodium sulfate were added. The samples were shaken and allowed to stand for 3 hours. The hexane was then decanted into a Kuderna-Danish evaporator. This extraction was repeated twice more with 50 ml of hexane, and extracts were combined with the original. The extract was taken to near dryness on a steam bath using a three-ball Snyder column and rediluted to an exact volume. The extraction procedure used in this experiment was a modification of that of Reed and Priester (*4*). Sensitivity of the method allowed for detection of each compound at 0.01 ppm.

A 5 $\mu$l of column injection was made from dilutions ranging from 1 ml to 50 ml of the residues redissolved in hexane. Determinations of residues were made using a MicroTek 220 gas chromatograph equipped with an electron capture (tritium) detector and a flame photometric detector.

Instrument parameters were as follows:

| | |
|---|---|
| Column: | Glass, 6′ x ¼″, packed with 1.5% OV-17/1.95% QF-1 on Chromosorb W 100/120; DMCS, HP |
| Carrier gas: | Repurified nitrogen at 60 ml/min |
| Temperatures: | Inlet 230° C |
| | Column 200° C |
| | Transfer 235° C |
| Detectors: (A) | Electron capture (tritium) Temperature 205° C |
| (B) | Flame photometric |
| | 1. Temperature 225° C |
| | 2. Mode—sulfur and phosphorus |
| | 3. Gas flows: Helium-200 ml/min; oxygen-20 ml/min; Air-100 ml/min; nitrogen-60 ml/min |

The 1.5% OV-17/1.95% QF-1 column was efficient in resolving the parathion and endosulfan peaks and thus was used for both detectors. As the sensitivity of the electron capture detector is greater, it was used for quantitation of the peaks on the basis of relative peak heights. The flame photometric detector was used for confirmation of compounds detected. The two endosulfan isomers were quantitated independently but reported as total endosulfan.

Recoveries averaged 92.6% for parathion and 87.3% for endosulfan. Results were not corrected for recovery.

### *Results and Discussion*

Fig. 1 presents parathion residue levels in relation to application time. Within the framework of this experiment regarding temperature, moisture, and sunlight, the maximum time required for parathion to degrade to "zero" levels was estimated to be 7 days and the min-

TABLE 1.—*Parathion and endosulfan residues on field-treated tobacco, South Carolina—1971*

| Application Date | Sampling Time in days from last application | Mean Residual Level in ppm of Four Replicates per Treatment | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Parathion (1.5 A.I. lb/acre) | | Endosulfan (.5 A.I. lb/acre) | | Parathion (1.5 A.I. lb/acre)/ Endosulfan (.5 A.I. lb/acre) | | Control | |
| | | Parathion | Endosulfan | Parathion | Endosulfan | Parathion | Endosulfan | Parathion | Endosulfan |
| June 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 1 | .619 | .161 | .108 | .905 | 1.049 | 1.489 | .140 | .091 |
| | 10 | .146 | .195 | .144 | .459 | .146 | .305 | .091 | .069 |
| June 21 | 1 | .436 | .076 | .009 | .695 | .736 | 1.189 | .041 | .100 |
| | 3 | .091 | .224 | .130 | .234 | .159 | .231 | .091 | .221 |
| | 5 | .069 | .106 | .071 | .152 | .070 | .174 | .089 | .072 |
| | 9 | .017 | .056 | .012 | .156 | .014 | .148 | .020 | .067 |
| | 15 | .004 | .037 | .003 | .077 | .007 | .106 | 0 | .052 |
| July 8 | 1 | 1.123 | .679 | .380 | 1.751 | 1.304 | 1.741 | .584 | .529 |
| | 4 | .632 | .418 | .169 | .969 | .694 | .954 | .493 | .389 |
| | 8 | 0 | .145 | .062 | .311 | 0 | .235 | 0 | .147 |
| | 18 | 0 | .047 | .002 | .207 | 0 | .174 | 0 | .037 |

NOTE: $LSD_{05}$ = least significant difference at 95% probability level = .166 for parathion and .363 for endosulfan; residues were not corrected for percent recovery (see methods).

imum time 2 days. "Zero" levels are considered within the limits of actual zero, i.e., undetectable amounts, plus the calculated least difference considered statistically significant at the 5% level of significance.

Similar information is provided for endosulfan in Fig. 2 and indicates reductions of residues to "zero" in 10, 2, and 7 days, respectively, after three successive pesticide applications.

Although the experimental design included guard rows, there were still measurable amounts of drift of the insecticide between all plots. Table 1 lists the actual amounts of each insecticide detected in each of the four treatments. In most instances, the contaminant or "drifted" chemical (e.g., endosulfan detected in the parathion treatment) was less than the $LSD_{.05}$. Thus, it is felt that experiment safeguards such as guard rows and control plots were highly effective in reducing the contamination between plots.

The parathion-endosulfan treatment was included to determine if any interaction existed between the two chemicals. It was found that more parathion residue was present when endosulfan was present; however, the converse was not true as can be seen from Tables 1, 2, and 3.

FIGURE 1.—*Average parathion residues on tobacco leaves*

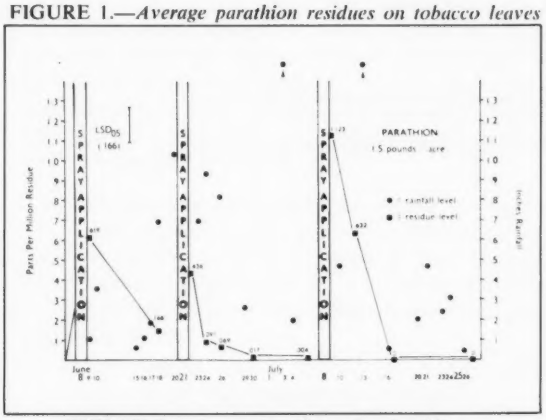


FIGURE 2.—*Average residues of endosulfan on tobacco leaves*

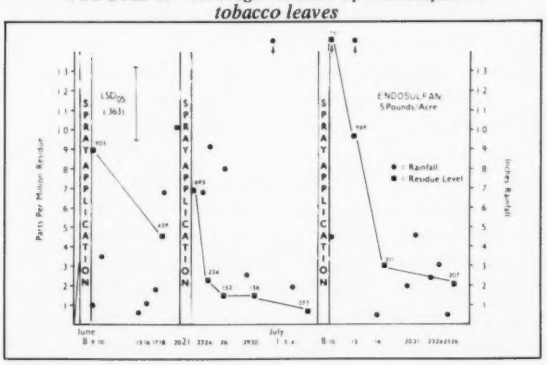


TABLE 2.—*Analysis of variance for the variable parathion*

| Source of Variation | Degrees of Freedom | Sum of Squares | Mean Square | F |
|---|---|---|---|---|
| Treatment | | | | |
| Parathion | 1 | 1.8217 | 1.8217 | 100.765** |
| Total Endosulfan | 1 | .0282 | .0282 | 1.559 |
| Para x Endo | 1 | .1884 | .1884 | 10.421** |
| Error (a) | 12 | .2169 | .0181 | |
| Time | 11 | 12.9523 | 1.1775 | 81.665** |
| Ti x Para | 11 | 4.0406 | .3673 | 25.476** |
| Ti x Endo | 11 | .2898 | .0263 | 1.827* |
| Ti x Para x Endo | 11 | .4412 | .0401 | 2.782** |
| Error (b) | 132 | 1.9032 | .0144 | |

*$P < .05$
**$P < .01$

TABLE 3.—*Analysis of variance for the variable endosulfan*

| Source of Variation | Dergees of Freedom | Sum of Squares | Mean Square | F |
|---|---|---|---|---|
| Treatment | | | | |
| Parathion | 1 | .1201 | .1201 | 1.034 |
| Total Endosulfan | 1 | 6.3731 | 6.3731 | 54.873** |
| Para x Endo | 1 | .0178 | .0178 | .154 |
| Error (a) | 12 | 1.3937 | .1161 | |
| Time | 11 | 21.1820 | 1.9256 | 27.939** |
| Ti x Para | 11 | .5584 | .0508 | .737 |
| Ti x Endo | 11 | 8.0654 | .7332 | 10.638** |
| Ti x Para x Endo | 11 | .6309 | .0574 | .832 |
| Error (b) | 132 | 9.0979 | .0689 | |

**$P < .01$

In excess of 12 inches of rain fell during the period of the experiment, and it is felt that the unusual rainfall may have physically effected some residue reduction. Daily temperature means averaged 80.9° F with a standard deviation of 2.3 and a range of 76° to 85° F.

This experiment should be repeated for confirmation purposes and to observe results under different environmental conditions including different moisture conditions to determine effects of weather on degradation.

See Appendix for chemical names of compounds discussed in this paper.

This study was supported by Environmental Protection Agency Contracts, Numbers PH21-2017 and 68-03-0045.

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# APPENDIX

## *Chemical Names of Compounds Discussed in This Issue*

| | |
|---|---|
| ALDRIN | Not less than 95% of 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene |
| BHC | 1,2,3,4,5,6-hexachlorocyclohexane, mixed isomers |
| CHLORDANE | 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane |
| DDE | 1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethylene |
| DDT (including its isomers and dehydrochlorination products) | 1,1,1,-trichloro-2,2-bis(*p*-chlorophenyl)ethane; technical DDT consists of a mixture of the *p,p'*-isomer and the *o,p'*-isomer (in a ratio of about 3 or 4 to 1) |
| DIELDRIN | Not less than 85% of 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8a-octahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene |
| ENDOSULFAN (THIODAN®) | 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide |
| ENDRIN | 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-endo*-5,8-dimethanonaphthalene |
| HCB | hexachlorobenzene |
| HEPTACHLOR | 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene |
| HEPTACHLOR EPOXIDE | 1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan |
| LEAD | Pb |
| LINDANE | 1,2,3,4,5,6-hexachlorocyclohexane, 99% or more gamma isomer |
| MERCURY | Hg |
| MIREX | dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[*cd*]pentalene |
| PARATHION | *0, 0*-diethyl *0*-*p*-nitrophenyl phosphorothioate |
| PCP | pentachlorophenol |
| POLYCHLORINATED BIPHENYLS (PCB's) | Mixtures of chlorinated biphenyl compounds having various percentages of chlorination |
| TDE (DDD) (Including its isomers and dehydrochlorination products) | 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; technical TDE contains some *o,p'*-isomer also |

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